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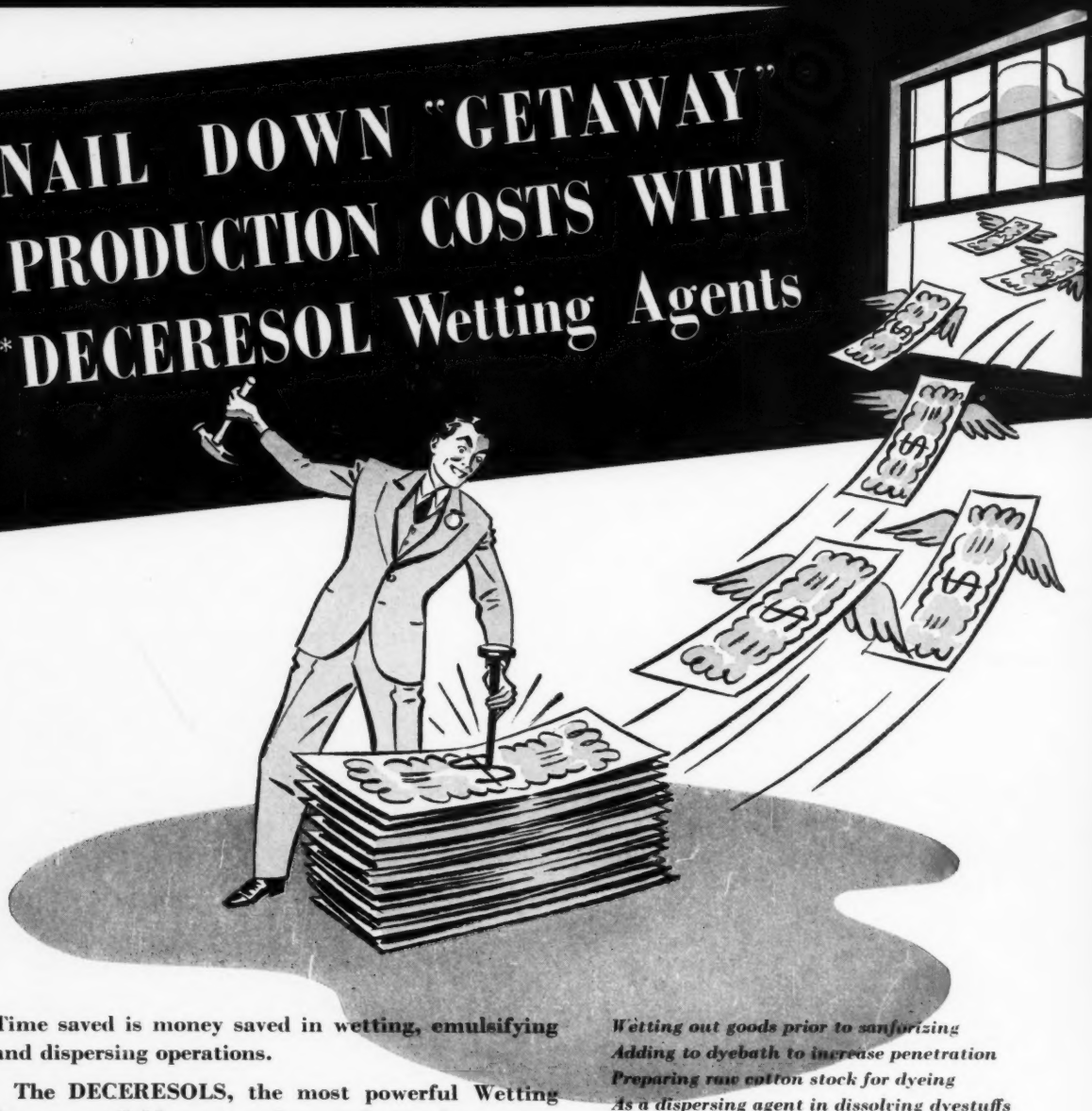

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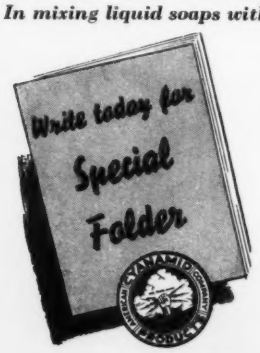

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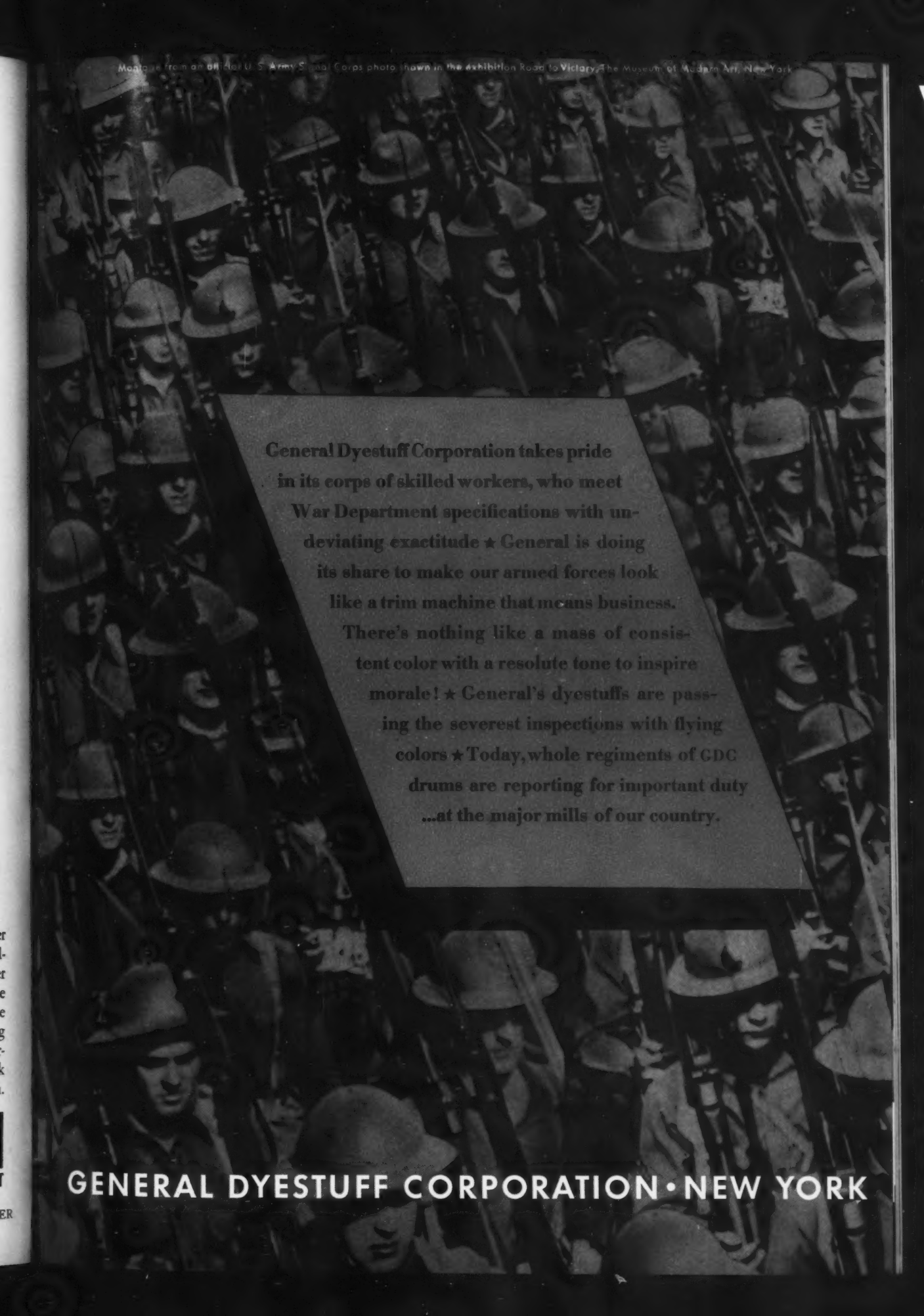
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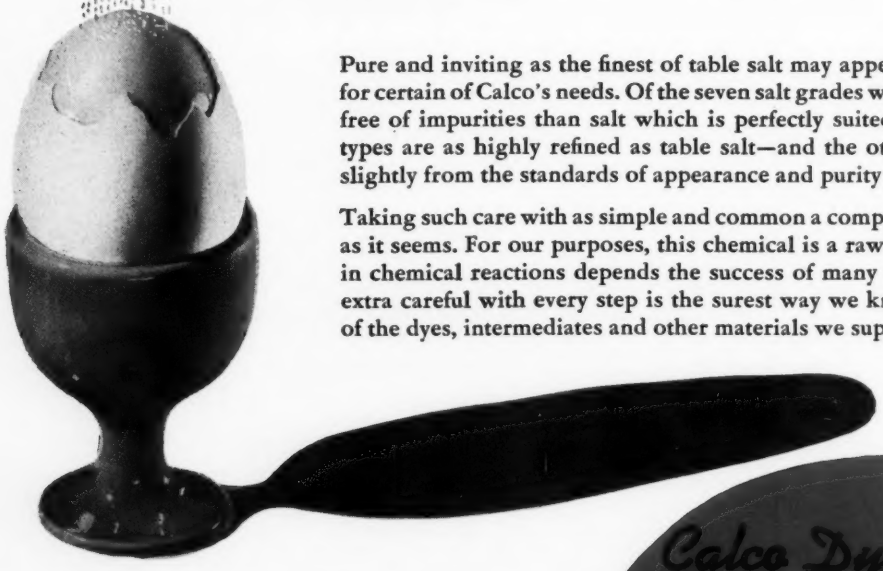

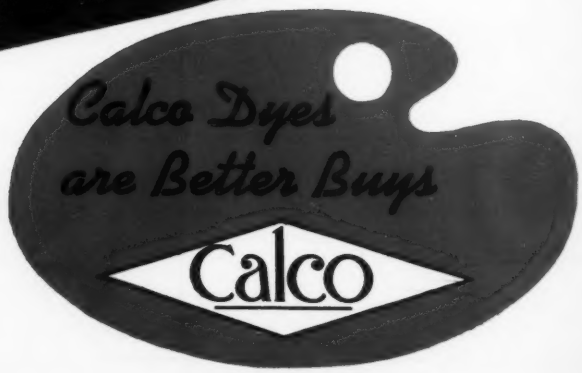

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VOLUME 31 AUGUST 3, 1942 NUMBER 16

High Polymeric

CHEMISTRY OF FIBERS

Made by Carothers

HERMAN BOXSER

RECENT developments in the field of organic chemistry which have produced truly synthetic fibers, such as nylon and Vinyon, have caused the average textile chemist to refer to recent editions of organic chemistry text books. This has been necessary in order to review those phases of the organic field which embody some of the new phenomena which have been divulged in the production of these new truly synthetic fibers.

Until recently, before the advent of nylon, the chemistry of the so-called synthetic fibers, or rayons, was rather simple. In the case of the regenerated celluloses, cellulose from wood pulp or cotton linters was the starting point. It was first dissolved in an alkaline medium, as in the viscose process, or in a cuprammonium solution, as in the Bemberg process, and the dissolved cellulose reprecipitated in the form of a fiber, after passing through a spinneret into an acid precipitating bath. In the case of cellulose acetate fiber, the final fiber possessed a different chemical structure from that of cellulose, but nonetheless the chemical reaction was comparatively simple.

With the discovery and development of nylon, there appeared in chemical and textile literature, a new group of terms—namely, "polymerization," "polymers," "superpolymers," "condensation" products, etc. These terms were very akin to those used in describing some of the processes for making synthetic resins. It was only natural, therefore, for the textile chemist to open his text book on organic chemistry in order to obtain further clarification of some of these new terms and processes. Unfortunately the average text book, especially the older editions, have revealed but scant information on the subject of higher polymeric chemistry.

It is the opinion of the writer that no author has clarified more thoroughly the description of this new field of chemistry—high polymeric chemistry—than the person who discovered nylon itself—Wallace Hume Carothers. In the following paragraphs we will attempt to interpret Carothers' descriptions of the various reactions involved, in those phases of the chemistry of high polymers, which resulted in the discovery of the polyamide—nylon. Our bibliography has been "The Collected Papers of Wallace H. Carothers on Polymerization" edited by Mark and Whitby.*

Polymerization has been defined by Carothers as the chemical union of many similar molecules, either with or without the elimination of simpler molecules such as H_2O, HCl, NaCl, NH_3, etc. He recognized the existence of two types of polymers, (1) A—(Addition) Polymers and (2) C—(Condensation) Polymers.

Before describing these we must first define the term monomer. A monomer is a molecule, or it may be a compound, containing only one structural unit. For example, ethylene oxide contains but one structural group—CH_2CH_2O.

A—polymers are produced by recurring addition of monomers. The molecular formula of the monomer is identical with that of the structural unit. The monomer, in turn, can be obtained from the polymer by thermal or photochemical decomposition. Simply, A—polymers are formed by self addition. As an example, we may consult Figure I, which shows the polymer Polystyrene, its monomer and the structural unit.

Here we note that the molecular formula of the structural unit is identical with that of the monomer. The

*Interscience Publishers, New York, 1940.

Figure 1

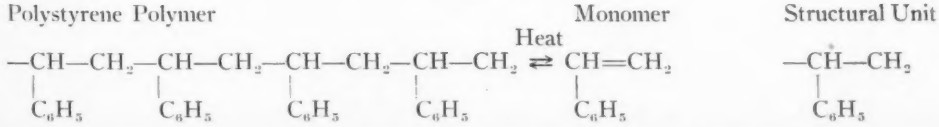


Figure 2

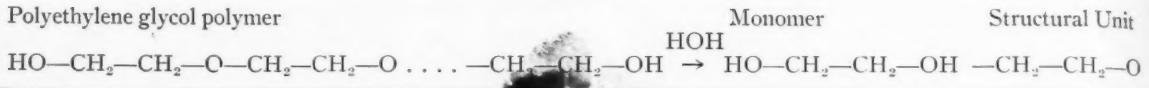
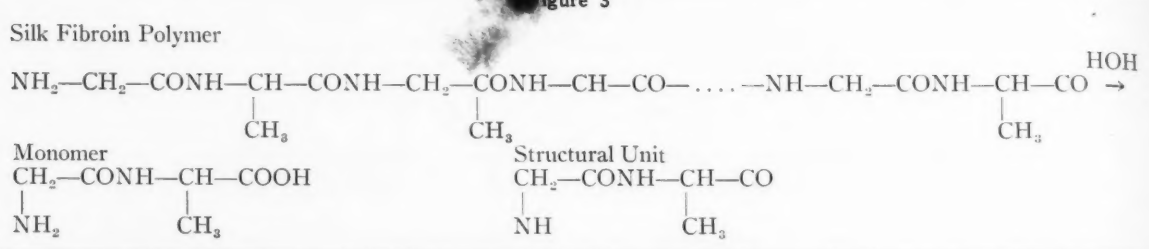


Figure 3



polymer may be transformed into the monomer merely by heating and the reverse transformation—polymerization—occurs spontaneously—i.e., by self addition or activation of the latter by the action of catalysts.

C—(condensation) polymers are produced by the recurring condensation or union of monomers. However, the molecular formula of the monomer differs from that of the structural unit. The monomer can be obtained from the polymer by hydrolysis and the polymer is formed by a reaction described by Carothers as a "polyintermolecular condensation."

The above paragraph may appear complex, so we will clarify this with the following example (Figure 2). It will be noted that the molecular formula of the structural unit for polyethylene glycol differs from that of the monomer by H_2O. In other words, subtract HOH from the monomer and the formula for the structural unit results. Another example is silk fibroin (Figure 3).

Here again if we remove HOH from the monomer, we arrive at the above described molecular formula for the structural unit.

Degradation of the polymer to the monomer in both of the above reactions occurred by hydrolysis. Conversely, if we reverse the process and build up the polymer from the monomer, it would require the elimination of HOH, water, among many molecules. This type of polymerization, of which the preparation of nylon is one, was termed by Carothers "polyintermolecular condensation."

The simplest and perhaps the most numerous high polymers are the "linear polymers." They are characterized structurally by the fact that their molecules are long chains built up from a repeating radical or unit. This type of structure may be represented by the general formula—

—— A—A—A—A—A—A—A—A—A ——

As mentioned previously, the repeating radical —A— is called the structural unit. The number and nature of these units determine the nature of the final molecule. Usually to complete the formula it is necessary to specify the disposition of the terminal valences, which may be joined to form a cyclic structure or saturated by univalent groups. Whether the chain is open or closed, polymers of this class are called "linear polymers." It should be added that linear high polymers are usually mixtures containing chains of different lengths.

Thusly, if the polymer is derived from a single compound, the structural units of the chain will in general be identical, but the mutual reaction of two or more compounds that are chemically similar but not identical may lead to chains made up from two or more different units. Such products are called "linear mixed polymers."

Carothers found that there was a definite relationship between the molecular weights of linear polymers and their melting points. Usually the melting point increases with the cohesive force (polarity) of the structural units.

The melting point usually increases with an increasing molecular weight up to a certain point, and after that it remains unchanged even though the molecular weight be increased many fold. Polyamides (in which class nylon falls) have much higher melting points than analogous polyesters. (Polyesters may be derived from the interaction of dibasic acids and glycols).

Linear polyesters whose molecular weights lie below 5,000 are definitely crystalline. Those whose molecular weights lie above 10,000 show evidences of crystallinity which are far more vague.

In attempting to produce polymers of high molecular weights resulting from condensation reactions, Carothers was hampered by the limitations of the molecular stills that had been developed until the period preceding his work with high polymers. For clarification, we may describe a molecular still as a distilling apparatus in which polymers of high molecular weights may be produced by either self combination or by elimination of some volatile product.

Investigators have shown that the tendency to distill diminishes with increasing molecular weight, and substances of high molecular weight are completely non-volatile. There are instances of reversible reactions in which a volatile and non-volatile substance both result, and these reactions can be forced to completion by causing the volatile product to distill from the reaction mixture as fast as it is formed. The size of molecules produced depend upon the completeness of the reaction. With the aid of a molecular still one can obtain products of much higher molecular weights than with the ordinary distillation equipment, by

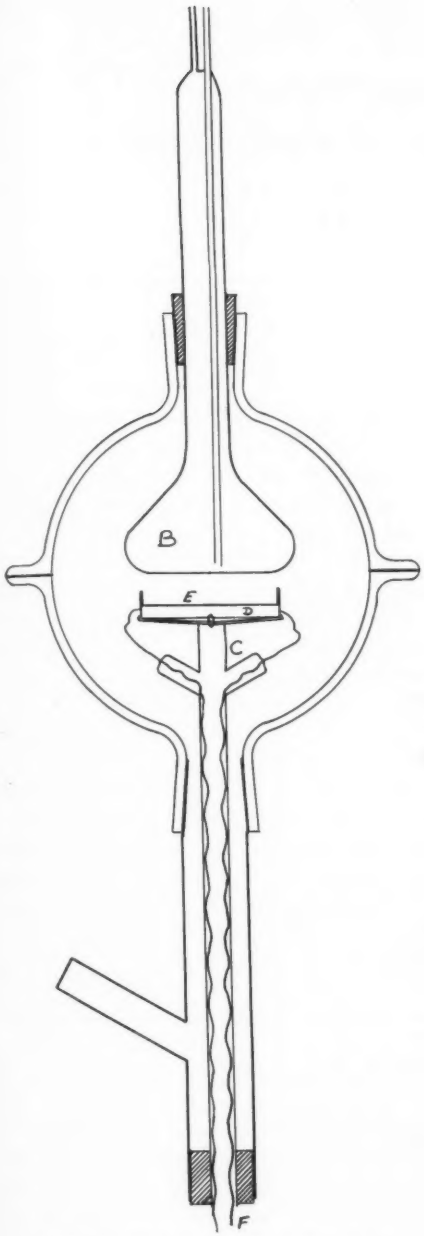


Fig. 4—Molecular Still of Carothers.

causing the above described type of reaction to go to completion.

If Figure 4 is consulted, there will be found a sketch of the molecular still in which improvements by Carothers have been incorporated. The whole system, first, is highly evacuated. (B) is the condenser containing water leads for cooling. (C) is the glass support for the heater (D) and the distilling pan (E). The heater and distilling pan are contained in an outer copper pan. The heater leads (F) are brought up through the support (C).

Carothers' improvements introduced the pan and its proximity to the condenser. The increased efficiency resulted in the complete removal of the volatile product as most of the molecules that managed to escape from the evaporating surface were caught by the condenser with a negligible probability of return.

High polymers are used extensively as structural materials in the construction of such substances of economic importance as cellulose, silk, nylon and rubber. Their uses depend upon such properties as mechanical strength, toughness, pliability and elasticity. Such properties are found to a useful degree only among polymers of high molecular weight.

The qualities necessary for a useful fiber appear to be associated with a very high molecular weight linear polymeric structure and a certain degree of crystallinity, or definite order in the arrangement of the molecules.

In natural cellulose, or in the silk fiber, the long molecular chains are arranged in an ordered fashion parallel with the fiber axis. This arrangement provides the maximum possible strength in the direction of the fiber axis since the mutual cohesive force of the long chains is fully utilized. To rupture the fiber it is necessary to cause the chains to slip past one another against this cohesive force.

The strength of a rayon filament can be increased several fold by the action of stress, while it is in the spinning bath, and a comparison of the X-Ray patterns shows a much higher degree of orientation along the fiber axis in the filament formed under stress.

The peculiarities of high polymers are nowhere more strikingly exemplified than in their curious ability to accept permanent orientations through the action of mechanical stress. Very large molecules are not capable of adjusting themselves instantly to any changes in physical environment, and the properties of a very high molecular weight material may vary over a wide range depending upon the physical treatment it has received.

Fiber strength was found to depend upon molecular length, for experiments indicated that it was not possible to spin continuous filaments from certain polyesters until their molecular weights reached 7,000.

A spectacular phenomenon which Carothers called "cold drawing" was exhibited in connection with the formation of fibers from these polyesters. If stress was gently applied to a cylindrical samples of the opaque and unoriented polyester at room temperature, instead of breaking apart, it separated into two sections joined by a thinner section of the transparent oriented fiber. As pulling was continued this transparent section grew at the expense of the unoriented sections until the latter were completely exhausted.

A remarkable feature of this phenomenon was the sharpness of the boundary at the junction between the transparent and the opaque sections of the filament. During the drawing operation the shape of this boundary did not change. it merely advanced through the opaque sections until the latter were exhausted. (See Figure 5.) It was found that this operation could be carried very rapidly

(Concluded on page 394)

ELASTICITY OF WOOL

as Related to its Chemical Structure*

MILTON HARRIS, LOUIS R. MIZELL, and LYMAN FOURT

Research Associateship of the Textile Foundation at the National Bureau of Standards, Washington, D. C.

ABSTRACT

Wool is of particular value in those branches of the textile industry that manufacture apparel, fabrics, blankets, carpets, and felts—commodities which are important because of their warmth or their elasticity; that is, their ability to regain their original lengths or shapes after they have been distorted. Actually, this elasticity is primarily responsible for the warmth of wool, in that it allows the fabric to maintain a porous structure. The small air spaces in such a structure impart to the fabric its insulating properties. Thus, a cotton blanket would be as warm as wool if, instead of matting together in use, it would maintain a porous structure as does a woolen blanket.

The basis of the elasticity of wool has been extensively investigated by Research Associates of the Textile Foundation at the National Bureau of Standards. It appears that wool owes its elasticity to a rubber-like molecular structure, the molecules being distinguished by their freedom to assume various shapes. This is in contrast to most of the other common fibers, which resemble a bundle of closely packed extended strings, each string representing a long molecular chain. When such fibers are distorted very much, these long chains move into new positions with respect to each other. Since in a fiber such as cotton the new positions are similar to the old, the fiber does not return to its original shape. The ease with which this can occur is one of the principal reasons why cotton and similar materials crease so readily. The molecules of wool fibers would also slide past one another and permanent distortion would be produced if they were not connected at intervals by short cross-chains which produce a three-dimensional or network structure. Thus, when wool is stretched or folded, the chains do not slide permanently out of position; rather, tensions are set up which cause the fiber to return to its original shape after the removal of the external force.

It is of interest to note that the function of the cross-chains in wool is very similar to that of the cross-chains which are presumably formed during the vulcanization of rubber. Indeed, the similarities between these materials are so striking that wool may in a sense be considered to be a vulcanized fiber, a respect in which it differs from all other textile fibers.

I. INTRODUCTION

THE earlier efforts of those engaged in research on textile fibers and more especially the regenerated or synthetic fibers were principally devoted to increasing their strengths. It is a matter of history that the first regenerated fibers were so weak, especially in the wet state, that they were considered by many to be a passing fad. The progress that has been made in the interim is well known; the strengths of many of these fibers have been increased to the point where they exceed the demands of many of the purposes for which they are now used.

This progress has resulted from numerous investigations, and in this connection, the early observations, by Sherrer[32] and by Herzog and Jancke[15] on ramie, and later by Meyer and Mark[26], Astbury and his collaborators[7] and others that the fibers show a predominant, preferred orientation, in which the molecules are alined more or less parallel to the axis of the fiber, were extremely helpful. The results of these investigations lead to the concept that fibrous materials, in spite of their lack of homogeneity and their high molecular weights, are not necessarily amorphous but show a definite crystallizing tendency, in that portions of the fiber apparently consist of compact bundles of long-chain molecules in a parallel arrangement. On the basis of this concept, it has been possible to explain many facts concerning the structure and strength of high-polymers in general and of the fibers in particular. For example, for a given fiber it has been frequently shown that the strength is directly related to the degree of orientation; that is, the more highly oriented the crystallites of the fiber the higher the strength. While it is recognized that other factors, such as molecular chain length and the nature of the intermolecular forces, also have a profound influence on the strength of fibers, it can be shown that in a general way the strengths of entirely different classes of fibers are comparable on the same basis. The data in Table 1 illustrate this point.

*This paper appeared in the July issue of *Industrial and Engineering Chemistry*.

TABLE 1
Comparison of Different Classes of Fibers

Fiber	*Relative Degree of "Crystallinity"*	*Breaking Strength Llbs./In.*
Flax	very high	up to 156,000
Ramie	very high	129,000-135,000
Nylon	high	72,500-100,000
Cotton	medium	40,000-111,000
Rayons*	low to high	22,000-110,000
Silk	medium	46,000- 74,000
Wool	low	17,000- 25,000

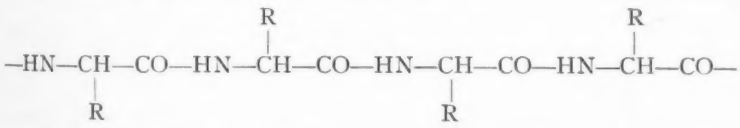
*Value depends on degree to which the rayon is oriented during manufacture.

Having achieved considerable success with respect to the production of fibers of high strength, many investigators have shifted their attention to the problem of trying to improve other mechanical properties of fibers. It appears that part of this trend has arisen from attempts to obtain fibers having "wool-like" qualities or properties. In view of this, it is pertinent to inquire into some of the properties which make wool different from other textile fibers. From the industrial point of view, the principal difference is found in the long-range elasticity of wool fibers; that is, their ability to recover from deformations of magnitudes considerably greater than those permitted by other types of fibers. The concept of orientation was effectively utilized in increasing the strength of the fiber, but, unfortunately, orientation is not directly correlated with long-range elasticity and accordingly, the understanding of this unique mechanical property of wool must be sought in some other feature of its molecular structure. It is the purpose of this paper to examine certain aspects of the molecular structure from the point of view of their relations to long-range elasticity as well as to strength.

II. THE MOLECULAR STRUCTURE OF WOOL

Wool is composed principally of protein substance and, accordingly, it appears appropriate at this time to consider the factors which may influence the mechanical properties of fibrous proteins in general and wool in particular.

Proteins are poly-condensation products in which the different amino acids are linked together to form the poly-peptide chain, shown in the following scheme:



The mechanical properties of such chains can be considered, in general, to depend on the following four factors:

(1) They exhibit great flexibility. This enables the protein molecule to assume a great number of possible configurations which could be either of the folded or spiral type. The importance of this molecular flexibility was first recognized by Astbury and Woods who in their earlier work on wool[6] preferred a rather specific type of fold for the molecules of the fiber in the unstretched state, which they referred to as the α-keratin configuration. The long-range extensibility of wool was ascribed to the opening of these folds into the more nearly straight chain configuration known as the β-keratin form. The original α-keratin configuration has been shown to be untenable by Neurath[27], and a new type of fold has now been proposed by Astbury and Bell[3]. Such structures have been suggested on the basis of the X-ray data, and should accordingly be found principally in the "cystalline" regions of the fiber. Since, as also is indicated by the X-ray diffraction patterns, these regions account for only a relatively small proportion of the total wool fiber, it appears that one may assume a more or less random type of folding in the "amorphous" regions which make up the bulk of the fiber. That a variety of configurations can exist is readily demonstrable by the construction of molecular scale models of polypeptide chains[38]. In considering the mechanical properties of wool it seems therefore that more attention should be directed to the less organized regions of the fiber than has heretofore been done. It would be expected, for example, that the extension process might manifest itself to a greater extent in the amorphous rather than in the crystalline regions, and that the increase in crystallinity obtained on stretching a fiber may result from orientation of the unoriented regions as well as from changes in the already-oriented portions of the fiber.

TABLE 2
Amino-Acid Composition of Wool

Amino Acid	*Present in Wool*	*Reference*	*Grams Residue per 100 Grams Wool*	*Grams Side-Chain per 100 g. Wool*
	Per Cent		*Grams*	*Grams*
Glycine	6.5	9	4.94	0.09
Alanine	4.4	22, 1	3.52	.74
Serine	9.41	23	7.80	2.76
Proline	6.75	22	5.69	2.46
Valine	4.72	22	3.99	1.73
Threonine	6.76	23	5.74	2.59
Cystine/2	12.72*	24	10.83	4.89
Leucine isomers	11.3	22	9.75	4.92
Aspartic acid	7.27	35	6.28	3.22
Lysine	3.3	31	2.89	1.63
Glutamic acid	15.27	35	13.40	7.58
Methionine	0.71	22	.62	.36
Histidine	.7	9	.62	.37
Hydroxylysine	.21	40	.19	.11
Phenylalanine	3.75	22	3.34	2.07
Arginine	10.4	41	9.33	5.97
Tyrosine	5.8	30	5.23	3.43
Tryptophane	0.7	9	.64	.45
TOTAL	110.67		94.80	45.37
Ammonia N	1.18	36	—.30	—.30
Total, corrected for ammonia N			94.50	45.07

*Based on 3.55 per cent total sulfur, subtracting methionine sulfur.

In conclusion, (2) They possess a large number of the highly polar peptide linkages which can give rise to inter- and intramolecular hydrogen bonding. While these bonds contribute much towards increasing the strength of the fiber, such close spacings of these groups along the molecular chain would be detrimental to other desirable fiber properties, were it not for another factor discussed in the following section. Carothers and Hill[11] have demonstrated that a

preponderance of polar groups in synthetic materials renders linear polymers non-flexible and brittle.

(3) They contain relatively large side chains (R groups in the scheme of the polypeptide chain) which prevent close packing of the protein molecules and thus decrease the extent to which hydrogen bonding can occur. In wool, nearly all of the constituent amino acids are of the type having large side chains, as shown by the data in Table 2. From these data it can be estimated that close to 50 per cent of the weight of wool is in the side chains. Close packing of molecular chains composed of such amino acids would indeed be difficult and intermolecular hydrogen bonding would be minimized. It would accordingly be expected that wool fibers would exhibit relatively low tensile strengths, an expectation which is borne out by experiment (Table 1). It should be pointed out, however, that wool fibers would exhibit even lower tensile strengths were it not for the presence of covalent cross-links (discussed in the following section) between the molecular chains.

(4) They exhibit association forces other than those contributed by hydrogen bonds. These may arise from various sources, but in the present discussion only those contributed by the amino acid cystine, which is found in unusually large amount in wool and other mammalian hair fibers, will be considered. Cystine, as first suggested by Astbury and Street[5], is responsible for a considerable amount of covalent cross linking in the fiber. More recently, new chemical evidence[28] has been offered which supports the original conclusion of Astbury and Street. Wool may thus be considered a network of polypeptide chains linked together by the disulfide groups of the amino acid, cystine. Such a concept suggests that the role of cystine in wool must be an important one, and indeed it has been shown that many of the chemical, physical, and biological properties of wool protein[12, 13] are dependent on the presence of these cross-links. The importance of these cross-links becomes even more apparent in the subsequent discussion in this paper concerning the experimental alteration or rupture of these links.

III. EXPERIMENTAL PROCEDURES

1. Preparation of Chemically Modified Wools

The wool fibers used in the present study were a portion of a lot used in previous investigations in this laboratory and had been subjected to no chemical or mechanical treatment other than successive extraction with alcohol and ether followed by washing with water at 40° C.[33]

The preparation of chemically-modified wools in which the mode of linkage of the sulfur has been altered, without visibly affecting the fiber structure, has previously been described in detail[28]. The methods involve the reduction of wool with thioglycolic acid solution, followed by treatment of the reduced product with an alkyl halide. The reactions appear to affect only the disulfide groups of the cystine in wool and may be represented by the following equations:

$$W\text{—}S\text{—}S\text{—}W + 2HS\text{—}CH_2\text{—}COOH \rightarrow 2W\text{—}SH + (S\text{—}CH_2\text{—}COOH)_2 \quad (1)$$

$$W\text{—}SH + RX \rightarrow W\text{—}SR + HX \quad (2)$$

$$2W\text{—}SH + (CH_2)_nX_2 \rightarrow W\text{—}S\text{—}(CH_2)_n\text{—}S\text{—}W + 2HX \quad (3)$$

where W represents the portions of the wool connected by the disulfide groups, R represents an alkyl group, and X, a halogen atom. Reactions 1 and 2 result in a permanent rupture of covalent cross linkages. Reactions 1 and 3 result in the formation of new cross-links in which the sulfur atoms of the cystine are connected by short hydrocarbon chains.

2. Determination of Elasticity

Measurements of the elastic properties were made on individual fibers by a modification of the method described earlier[33]. In this method the 30 per cent index is the energy required to stretch a fiber to 30 per cent elongation after a treatment, divided by the similar energy requirement prior to the treatment. This index is based on Speakman's demonstration that wool fibers can be elongated 30 per cent without producing permanent deformation or weakening[34], if the duration of the strain is short. In the former investigations from this laboratory, however, the stress-strain characteristics of fibers were determined only during the extension process. In the present work, this procedure was modified so that measurements of the behavior of the fiber during its retraction could also be obtained.

The interpretation of these experiments involves four considerations, of which the first is the fraction of the original covalent bonds which has been altered. This may be inferred from the change in the percentage of cystine, which was determined by Sullivan's method[37] as used in this laboratory[14]. The cystine content of the untreated wool was 12 per cent, and in the modified wools varied downwards to 1 per cent or less. The second consideration is the resistance to extension, which can be conveniently referred to as strength. The third is the completeness of recovery in the unloading or retraction part of the stress-strain cycle. The fourth is the time function, which involves both the rate of change of stress and the effect of internal structure on viscosity. Experiments are now in progress to analyze these kinetic relations more directly.

IV. THE ELASTIC BEHAVIOR OF WOOL AND CHEMICALLY-MODIFIED WOOLS

Figure 1 shows the behavior of a typical wool fiber during two successive stress-strain determinations. The fiber was allowed to relax for approximately 24 hours between the first and second extensions. It is noteworthy that the entire stress-strain cycle is reproducible. This fact makes it possible to compare the stress-strain characteristics of a particular fiber in retraction as well as in extension, before and after a modification of its chemical structure.

When the cross-linkages have been permanently rup-

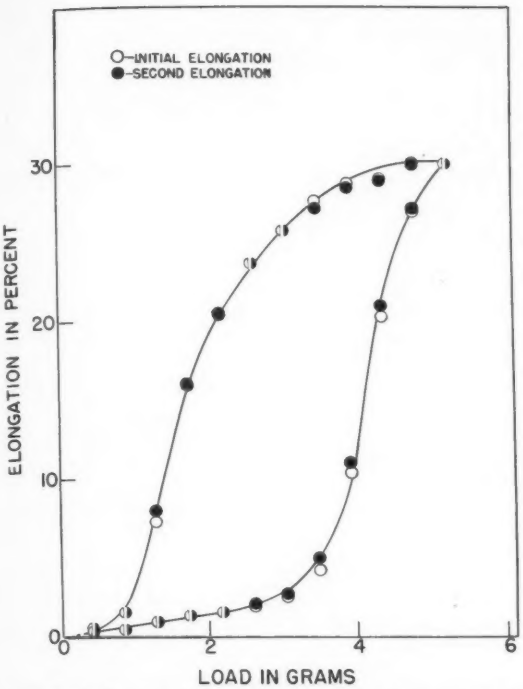


Fig. 1—Typical untreated wool fiber during two stress-strain cycles, separated by 24 hours. 30 per cent index = 0.99.

tured by the reduction process, followed by alkylation of the sulfhydryl groups with an alkyl monohalide of low molecular weight such as methyl iodide or ethyl bromide, the resistance to extension is greatly altered, as shown in Figure 2. Much less energy is required to elongate the

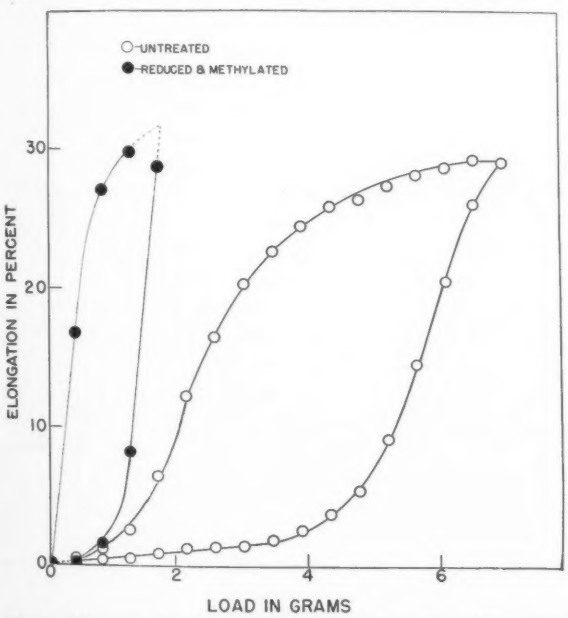


Fig. 2—Effect on the stress-strain cycle of opening 5/6th of the cross-linkages by reduction and alkylation with methyl iodide. 30 per cent index = 0.26.

fiber after the cross-links have been split, the 30 per cent index falling to the low value of 0.26. In this material the S-shaped curve, characteristic of the original wool fiber and of other highly elastic materials, is not observed in extensions to only 30 per cent, but can be demonstrated in experiments involving higher extensions. The whole scale of the relations of stress to strain has been shifted toward greater extensions for smaller forces. It should be added that the recovery from 30 per cent extension to the original length is complete and rapid.

If, after reduction, the cross-links are largely rebuilt by reoxidation of the sulfhydryl groups to the disulfide form, the wool recovers to a large extent its original properties, as shown in Figure 3. The small discrepancy may arise

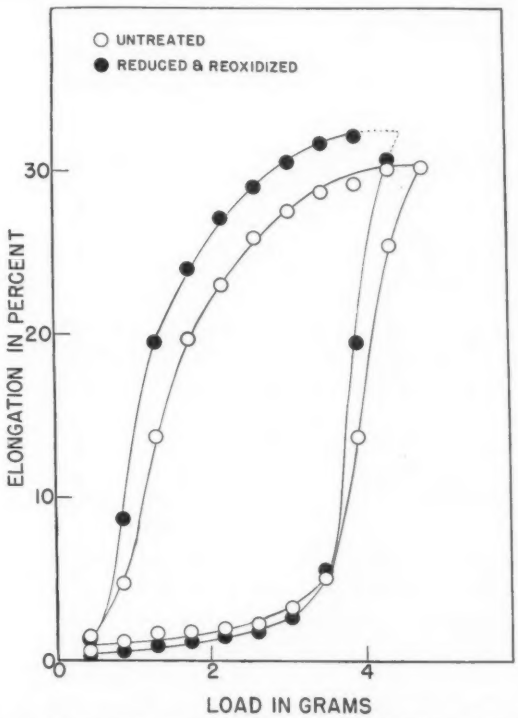


Fig. 3—Effect on the stress-strain cycle of reduction of one-half of the cross-linkages, followed by rebuilding by oxidation with oxygen. 30 per cent index = 0.96.

either from the possibility that reoxidation has not been complete or that a few SH groups had reacted, during the reoxidation, with the sulfhydryl groups other than those with which they were combined in the original fiber.

Alkylation of the reduced wool with an alkyl dihalide such as methylene bromide or trimethylene bromide results in the re-formation of cross-linkages, but in this case, the disulfide linkage has been replaced by a *bis*-thioether linkage of the type—$S(CH_2)_nS$—. While the position of the stress-strain curve for the fiber after such treatment has been slightly shifted (Figure 4) from that of the original fiber, the shape of the curve and the recovery are very similar to those of the original fiber. A slight shift in the position of the curve is to be expected, since, obviously, the lengths of the cross linkages have been increased and one would expect a slightly greater ease of extension of the fiber.

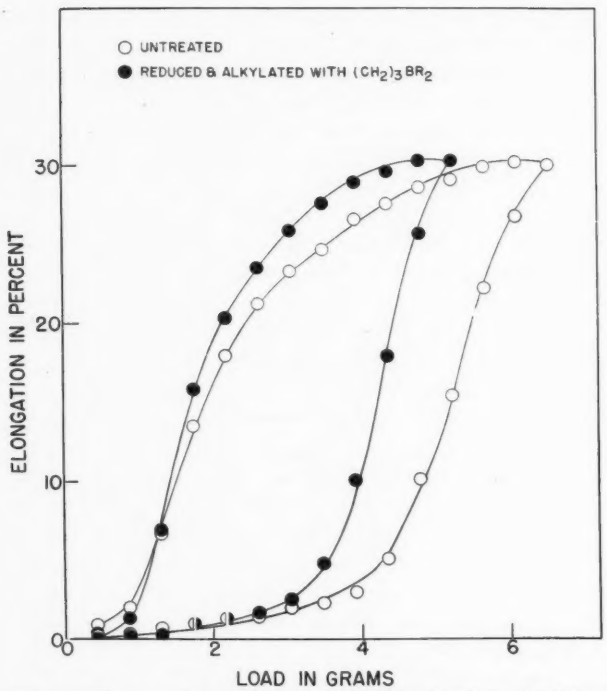


Fig. 4—Effect on the stress-strain cycle of rebuilding of 5/6ths of the cross-linkages as *bis*-thioethers by reduction and alkylation with trimethylene bromide. 30 per cent index = 0.82.

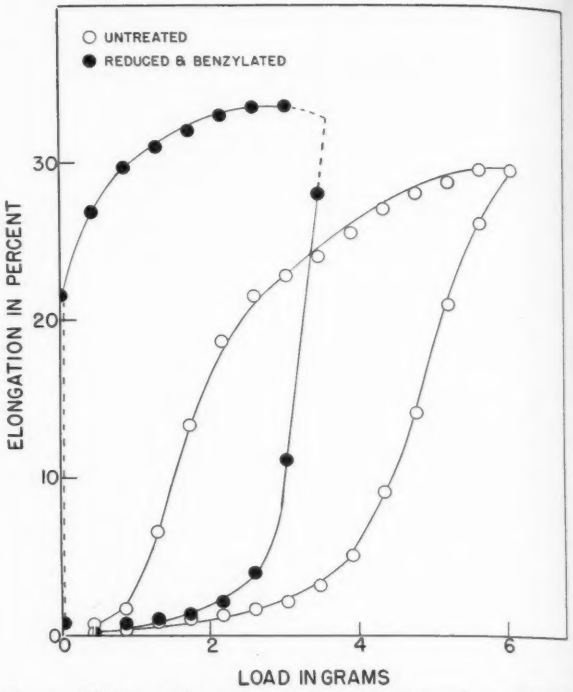


Fig. 5—Effect on the stress-strain cycle of opening of 5/6ths of the cross-linkages by reduction and alkylation with benzyl chloride. 30 per cent index = 0.65. The dotted line along the ordinate axis indicates a slow completion of the cycle by contraction at low stress.

Figure 5 shows the behavior of wool after reduction followed by alkylation with a large alkyl monohalide, benzyl chloride. Although in this case the covalent cross-linkages have been ruptured, the behavior of the fiber is very different from that of one in which covalent linkages have been ruptured by reduction followed by alkylation with small alkyl monohalides such as methyl iodide or ethyl bromide. As will be noted, the benzylated wool shows a considerably greater resistance to extension than the methylated wool (compare Figure 2). After sufficient load has been applied, the extension curve rises steeply with respect to the load axis. The relations with respect to time cannot be presented completely in this type of experiment, but it can be stated that the rate of flow is less than that of methylated wool. On removal of the load there appears to be a great resistance to the contraction of the fiber to its original length. Whereas in the other experiments presented here the elastic recovery was rapid and nearly complete within 1 minute after the removal of the last unit of load, in this experiment with benzylated wool retraction required 3 hours to reach an equal degree of completeness. This is indicated by the dotted line in Figure 5. The behavior is such as to suggest that while covalent cross-linkages have been broken, some interaction between the polypeptide chains still exists. It may be that benzyl groups on adjacent sulfur atoms exhibit mutual interaction of a van der Waals' type, or that there is an attraction between benzyl groups and a portion of a neighboring polypeptide chain. At the point of maximum extension the benzyl groups appear to form new interactions which resist the tendency of the fiber to return to its original length. An alternative explanation could be that the large volume of the benzyl group increases the energy of activation required for flow[20]. A quantitative investigation of the effects of both the size of the substituent and the temperature upon the flow is necessary for a more detailed explanation of these phenomena.

V. THE ANALOGY BETWEEN WOOL AND RUBBER

The results of the present investigation suggest that in many ways wool is quite analogous to rubber, and indeed in some respects may serve as a useful model for explaining certain properties of the latter.

It appears that the long-range extensibilities of both rubber and wool depend on the fact that both have configurations which can be straightened out during the stretching process[18]. Both wool and rubber are largely amorphous in the unstretched state although in this state the former appears to contain a somewhat higher proportion of a crystalline phase. As indicated by X-ray studies[19, 7], the amount of this phase is greatly increased during the process of stretching.

Probably the most interesting analogy, however, is found in comparing the properties of raw and vulcanized rubber with those of wool, before and after the rupture of its disulfide groups.* While it is generally assumed that vulcanization of rubber involves a cross-linking proc-

*Astbury and Dickinson have suggested that keratin is a "vulcanized" protein[4].

(Continued on page 392)

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AUGUST 3, 1942

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BACTERICIDAL RADIATION*

A. R. DENNINGTON

Lamp Division, Westinghouse Electric & Manufacturing Company

SCIENCE is gradually selecting and studying various groups of waves in the ether spectrum. These groups are studied for the purpose of finding their characteristics and their application to human welfare. While the ether spectrum extends to and beyond the infinitely short cosmic waves on one side and through the visible and heat regions and radio waves of various lengths on the other side, consideration is here given to a small group of waves in the ultraviolet region, Fig. 1.

Just as visible light is made up of different wavelengths which are separated by a prism into the rainbow colors, so the ultraviolet region may be separated into groups which have widely differing effects. Beyond the visible, the group of waves of 4,000 to about 3,300 angstroms are chemically active, affect photographic plates and, in common with still shorter wavelengths, cause fluorescent and phosphorescent materials to glow.

A second group measuring 3,300 to 2,850 angstroms are biologically effective causing erythemal and tanning reactions, increasing Vitamin "D" and preventing rickets. The effective bactericidal wavelengths 2,850 to 2,000 angstroms are receiving much attention during the past few years as the development of suitable generators makes possible the practical application of bactericidal radiations.

*Presented at meeting, Rhode Island Section, March 19, 1942.

Below 2,000 angstroms is a group of wavelengths which produce ozone in the air. A small proportion of these ozone producing waves, together with those in the region of 2,600 angstrom units which are more bactericidal in effect, produces the best conditions for the destruction of bacteria and mold.

EFFECT OF ULTRAVIOLET ON BACTERIA

In 1877, Downes and Blunt showed that bacteria are killed by sunlight. The lethal effect was attributed to mild and extended oxidation or, in short, to heat. Later, the killing effect was attributed to the production of hydrogen peroxide in the aqueous media. Both these early theories have been disproved by experiments in which the lethal effect was produced independently of heating or oxygen and the chemical action in the media was negligible. As a result of studies by Clark, Norton, and others, confirmed by Bayne Jones and Van der Lingen, it has been generally accepted that the bactericidal effect of selected wavelengths of ultraviolet is the result of direct photo chemical action on the organism. The disintegration of micro-organisms under radiations, principally of 2,537 angstroms, is shown in Fig. 2, where paramoecia, which are single cell organisms found in stagnant water, are exposed to the radiations from a Sterilamp. The picture shows how the radiations cause the organism to swell, blister and finally disintegrate.

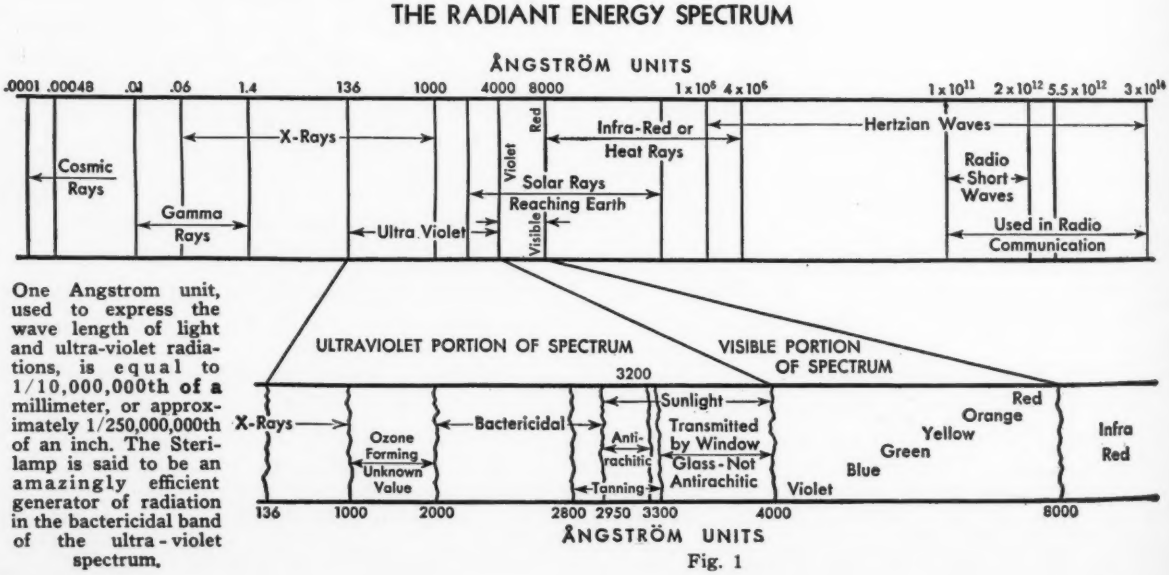

THE RADIANT ENERGY SPECTRUM
ÅNGSTRÖM UNITS
.0001 .00048 .01 .06 1.4 136 1000 4000 8000 1x10⁶ 4x10⁶ 1x10¹¹ 2x10¹² 5.5x10¹² 3x10¹⁴
Cosmic Rays
X-Rays
Gamma Rays
Ultra Violet
Violet
Red
Visible
Solar Rays Reaching Earth
Infra-Red or Heat Rays
Hertzian Waves
Radio Short Waves
Used in Radio Communication
One Angstrom unit, used to express the wave length of light and ultra-violet radiations, is equal to 1/10,000,000th of a millimeter, or approximately 1/250,000,000th of an inch. The Sterilamp is said to be an amazingly efficient generator of radiation in the bactericidal band of the ultra-violet spectrum.
ULTRAVIOLET PORTION OF SPECTRUM
VISIBLE PORTION OF SPECTRUM
3200
X-Rays
Ozone Forming Unknown Value
Bactericidal
Anti-rachitic
Tanning
Sunlight Transmitted by Window Glass-Not Antirachitic
Red
Orange
Yellow
Green
Blue
Violet
Infra Red
136 1000 2000 2800 2950 3300 4000 8000
ÅNGSTRÖM UNITS

Fig. 1

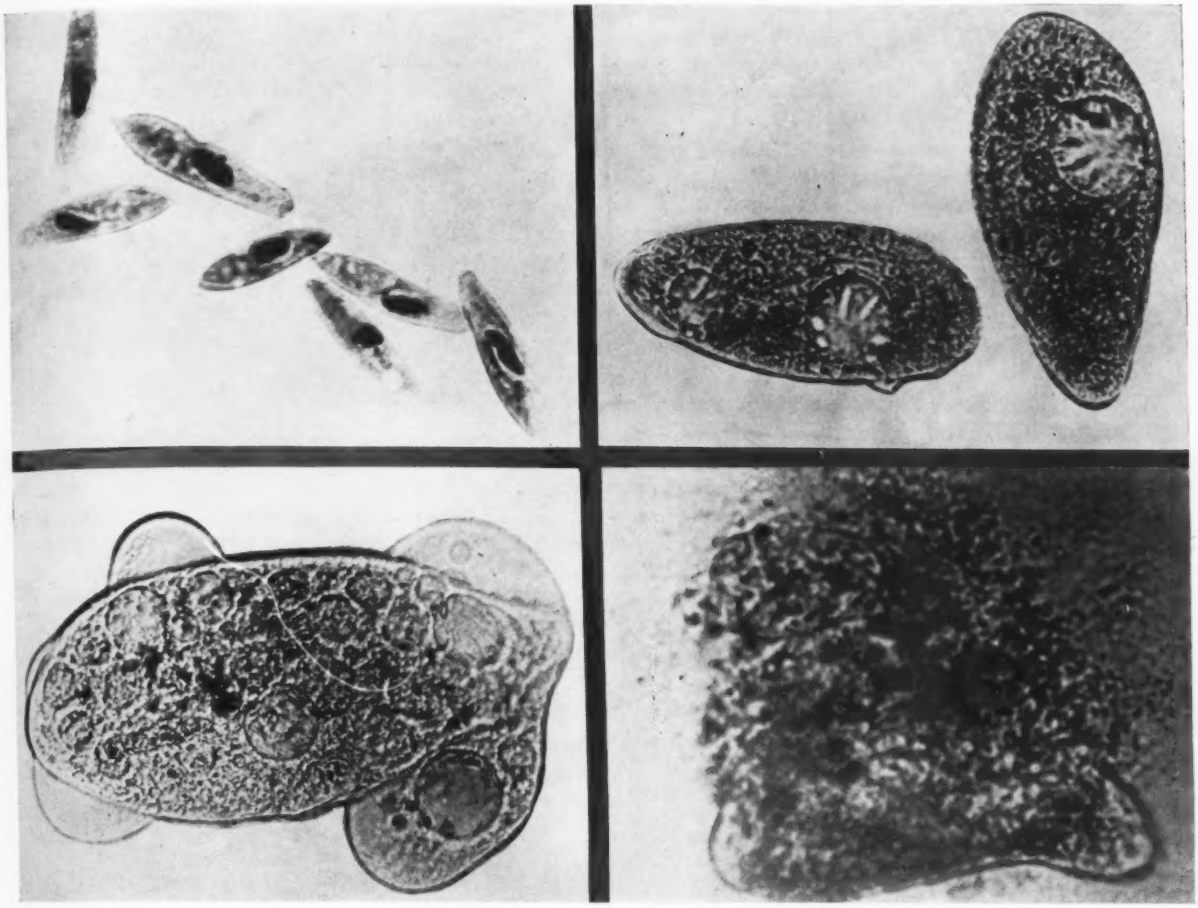


Fig. 2. Effect of bactericidal ultra-violet radiation on paramecia, single cell organisms, found in stagnant water and much larger than bacteria. Irradiation causes the organism to swell up, become covered with blisters and finally to disintegrate.

Bacteria are so small that the changes which take place due to irradiation cannot be shown clearly by an ordinary projection microscope, but, they are probably similar to the changes in the much larger paramoecia.

ULTRAVIOLET GENERATORS

The sun is considered the only natural source of ultraviolet but only a small part of the short wavelengths reach the earth, due to the filtering action of the atmosphere. The shortest wavelengths which can penetrate the atmospheric blanket measure about 2,900 angstroms and the amount of this radiation is only about one millionth as great as that at 3,130 angstroms. The ultraviolet radiation from the sun, in the bactericidal region, is great enough to have been noted, but, it is weak when compared to the output of many artificial sources.

Practically all artificial sources of ultraviolet radiation, with the exception of the carbon or iron electrode arc lamps, have one element in common, mercury vapor. Electrical discharges through mercury vapor produce more radiation in the ultraviolet region than similar discharges through any other known vapor or gas. The earliest and best known source of ultraviolet is the quartz mercury arc lamps, which has an envelope of fused quartz and at least one electrode of mercury. The output of ultraviolet can be shifted by varying the temperature and pressure of the mercury vapor. Increasing the temperature and pressure produces more of the longer wavelengths and the high pressure mercury lamp becomes an efficient source of visible light. If the pressure is kept low, measured by a few millimeters of mercury column, the radiation produced by an electric current is very largely in the bactericidal region, with maximum output at 2,537 angstrom units.

These low temperature, low pressure conditions are inherent in the Sterilamp, and make it an efficient bactericidal agent which is inexpensive to operate, has long life with small change in output, does not heat up the surrounding air and gives wide distribution of radiation. The glass tube which forms the lamp is made of glass which cuts off the radiation slightly below 2,000 angstroms, thus limiting the production of ozone so that the concentration does not rise to more than one part in three or four million parts of air. It is also true that radiation of 2,537 angstroms

breaks up ozone and thus acts as an automatic regulator of ozone concentrations. The slight amount of ozone developed is helpful in controlling the development of mold and bacteria in spaces which are shaded from direct radiation.

The electrical discharge in a Sterilamp is between unheated electrodes, because this permits simple construction of the lamp and the current controlling transformer, permits control of the output of the lamp by changing the primary voltage of the transformer, makes a lamp which will operate satisfactorily under varying temperature conditions and will have a long, effective life. Deterioration of output comes gradually due to changes in the glass known as solarization, and to a slight extent to blackening of the tube by vaporization of the electrode material.

MEASUREMENT OF ULTRAVIOLET

Much of the recent advance in the application of ultraviolet radiation is due to improvements in the equipment and methods for measuring the different groups of wavelengths in the ultraviolet spectrum. Three photo cells and a meter, (Fig. 3), developed by Dr. H. C. Rentschler, head

Fig. 3. Meter using different photo cells for measuring various portions of the ultra-violet spectrum. The instrument measures the quantity of radiation received during the time of exposure and registers the number of clicks. One click on the standard water meter equals 220 micro-watt seconds.

of Westinghouse Research Department, cover the principal groups of wavelengths in the ultraviolet spectrum. For measurement of the almost complete ultraviolet region, there is a photo cell having a thorium cathode which is responsive to a spectral range from 3,750 angstroms to about 2,000 angstroms with a maximum response at 2,600 angstroms. Another photo cell made up with a tantalum cathode responds to wavelengths from 3,000 to 2,000 angstroms with maximum sensitivity at about 2,400 angstroms. This photo cell is useful in measuring the bactericidal region of ultraviolet as it is not sensitive to the wavelengths near the visible edge of the ultraviolet spectrum. A third photocell with a platinum coated cathode is not affected by radiations above 2,000 angstroms, and therefore is capable of measuring the wavelengths which produce ozone in the air.

The ultraviolet radiations in the regions affecting these photo cells cause a minute electric current to flow through the tube and charge up a condenser which discharges through a relay tube. This in turn causes a larger condenser to discharge through the coil of a relay, which operates a counting mechanism with an audible click. After discharge the condensers again charge up, and the action is repeated as long as ultraviolet light reaches the electrodes and current flows through the photo cell. As each click represents a definite amount of ultraviolet radiation for which there is no generally accepted unit, the meter is called a "click" meter. Each click may represent any desired quantity of radiation by varying the size of the condenser in the circuit of the photo tube. However, the standard meter is calibrated so that one click represents 220 microwatt seconds.

Another small indicating meter is an adaptation of the foot candle meter. A filter, which cuts out about 95 per cent of the visible light but permits passage of ultraviolet, is placed over the window of the meter, and a fluorescent screen is placed next to the filter. Ultraviolet light which strikes the screen is converted into visible light and acts on the light sensitive cell which operates the pointer. This meter is very convenient for testing ultraviolet sources, such as the Sterilamp, which give off little heat, but it is not reliable for hot sources as the cell is sensitive to heat as well as light and the meter must be placed very close or in contact with the lamp to get a reading.

APPLICATIONS OF STERILAMPS

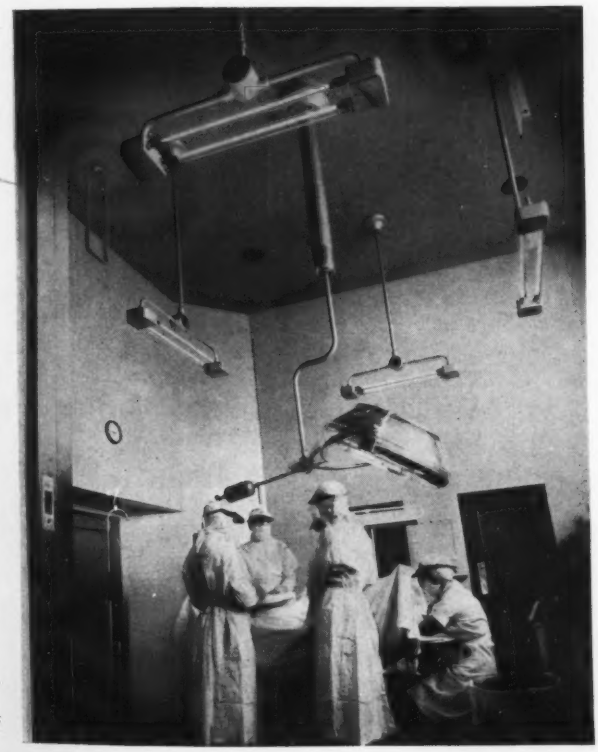
The development of an ultraviolet generator which operates at temperatures only a few degrees above the surrounding air, requires but a small amount of power, has a fairly uniform output and long life, opens up almost unlimited possibilities for usefulness. Early applications of Sterilamps were for the preservation of meat held in refrigerators. The radiations are effective in preventing or greatly reducing the development of mold and slime during the storage and marketing periods. Installations of Sterilamps in retail meat stores reduce trimming losses and in case of failure of the refrigeration equipment insure against meat spoilage until repairs can be made. Displays in refrigerated cases are protected from contamination by air-borne organisms and the sales appeal is strengthened. The meat packer and wholesaler use Sterilamps, Fig. 4, to keep their products free of organisms which cause spoilage and thus supply the retail trade with meat having low bacterial contamination and, consequently, of superior keeping qualities and flavor. Protection of meat in this way has made economically possible the tenderizing of beef in a few days at temperatures of 60° F. or more. Thus, only about one tenth of the time is required by this new

Fig. 4. Sterilamp installation in the cooling and packing room of a sausage manufacturer. The product keeps longer because it is cooled and packed in a room which is protected from bacteria and mold by bactericidal ultra-violet radiation.

and patented process compared to the former methods of aging at about 34° F.

In hospital operating rooms, Sterilamps are mounted over the operating table, Fig. 5, to reduce the danger of infection of surgical wounds by organisms floating in the air or exhaled by the operating staff. The records in more than 4,000 operations in one hospital show that in 1782 operations performed without radiation, 207 infections and 6 deaths resulted, while 2463 operations of the same types resulted in only 6 infections and no deaths. Time required for healing was also reduced by more than half.

Fig. 5. Sterilamp installation in a hospital operating room for the purpose of reducing the danger of infecting surgical wounds by air-borne bacteria. It is claimed that healing time and post-operative shock are reduced and that infections are almost completely eliminated.



In wards and nurseries the use of ultraviolet radiation has reduced spread of infectious diseases from person to person.

Evidence has also been accumulated to show that selected radiation in schools and offices has reduced or eliminated the spread of colds and other diseases which have a tendency to become epidemic.

Sterilamps have been applied in dairy barns, poultry houses, breweries, bottling plants, bakeries, pharmaceutical houses, air conditioning systems and many other places. A new industry has thus been developed that has as its primary purpose the protection of products and people from the unseen dangers ever present in the air. In textile mills Sterilamps are effective in many ways, for example to reduce bacteria in water supply, to irradiate and purify thin layers of materials piled upon each other to form felt, and to reduce the hazard of mildew and mold in storage rooms.

ONE HUNDRED AND THIRTY-EIGHTH COUNCIL MEETING

THE Council held its 138th meeting at the Chemists' Club in New York, on Saturday morning, June 27, 1942. Present were President Thomas R. Smith, presiding; Roland E. Derby and Charles A. Seibert, Vice-Presidents; William R. Moorhouse, Treasurer; Louis A. Olney, Chairman of the Research Committee; William H. Cady, Carl Z. Draves and P. J. Wood, Past Presidents; Dexter R. Kneeland and Clarence L. Nutting representing Northern New England; Frederic A. Prisley and Ben Verity representing Rhode Island; J. Ernest Meili and George A. Moran representing New York; William Ebersold, Arthur E. Jones and William A. Stringfellow representing Philadelphia; A. Henry Gaede representing Piedmont; Oliver G. Edwards representing Southeast; Kenneth H. Barnard, Chairman of the General Meeting Program Committee; Bertil A. Ryberg, Associate Research Director, and Harold C. Chapin, Secretary.

The Secretary's report of the 137th Council meeting and financial report of June 19, and the Treasurer's report of June 23, were accepted. Reports from the Treasurers of the Mid-West and Rhode Island Sections were approved.

It was voted that the President appoint a committee to consider revision of that part of Article X of the By-Laws concerned with financial allowances to local Sections. The Treasurer was instructed to invest $7,400 of general funds in National Defense Bonds of Series F. Appropriation was made for maintenance of the Secretary's office.

After consideration of reports from transportation authorities, it was voted that the General Meeting of

SECRETARY'S FINANCIAL REPORT—JUNE 19, 1942

	Applications	*Dues, Regular and Reinstate.*	*Dues, Corporate and Sustaining*	*Miscellaneous*	*Totals*
Received and transmitted to Treasurer					
August 1, 1941, to April 9, 1942	$1,412.50	$12,304.00	$5,337.50	$1,891.86	$20,945.86
April 9, 1942, to June 19, 1942	232.50	230.00	600.00	491.32*	1,553.82
Total in fiscal year to date	1,645.00	12,534.00	5,937.50	2,383.18	22,499.68
Leaving deposited by Treasurer with Secretary					$500.00

Miscellaneous items*

Year Books	$154.12
Reporters	12.20
Knitted tubing	50.00
Moth cloth	182.50
Dyed standards	15.00
Crock cloth	21.00
Buttons	4.50
Water test apparatus	7.50
Launderometer royalties	45.00
	$491.82
Less bank charges	.50
	$491.32

1942, planned for Atlantic City, be not held; and that thanks be extended to the Philadelphia Section for its efforts to extend every hospitality consistent with National defense. It was voted, however, that the Intersectional Contest be held, in manner to be devised by Mr. Barnard and his Program Committee, and that the papers be published.

The Greenville Finishing Co. was elected to Corporate membership. Each of the following was elected to the class of membership specified, as of thirty days from publication of application, provided no objection be received meanwhile by the Secretary:

Senior

A. I. Anderson	W. J. Hamburger	R. W. Redston
C. R. Atkins	J. F. Hardy	W. B. Reynolds
J. P. Bitter	C. Jones	H. Sandler
M. H. Boyce	H. C. Knight	H. G. Smith
J. A. Byars	W. R. Larson	F. M. Steadman
T. M. Chadwick	J. B. Mungall	F. A. Stetkiewicz
E. H. deVaudreuil	J. H. Murray	L. C. Voss
P. Doremus	W. E. Murray	D. B. Wicker
E. C. Dreby	R. A. Nelson	R. M. Wilson, Jr.
C. P. Dyer	J. Nerl	R. S. Withers
A. A. Gobeille	P. H. Netherwood	J. A. Woodhead

Junior

R. F. Hooper	W. Juda	R. G. Massingham
J. Jordan	H. W. Levi	J. Smith

Associate

J. E. Buonanno	E. E. Greene	J. N. Paradis
F. J. Cramer	H. A. Groban	F. E. Reardon
E. H. Endelson	M. P. Mulqueen	G. E. Robertson

Student

J. A. Arey, Jr.	S. Nulman	L. M. Vavala
H. R. Houghton	J. V. Perkins	C. K. Watson
R. M. Howorth	J. C. Rockett	N. Yao
D. Moss		

The following were transferred from other classifications to Senior membership—S. M. Cone, N. E. Daher, L. Gleklen, H. A. Green, H. H. Hatch, R. L. Jones, A. E. Koch, H. Liebmann, R. G. Yeaman.

Respectfully submitted,

HAROLD C. CHAPIN,
Secretary.

ANNUAL OUTING, NEW YORK SECTION

THE annual outing and golf tournament of the New York Section was held on Friday, June 19th, 1942, at the North Jersey Country Club, Paterson, N. J.

The program for the day included, in addition to the golf tournament, horseshoe pitching and a tennis tournament. The festivities concluded with dinner and entertainment. The dining room was filled to capacity. Prizes were awarded as follows:—

Golf—Members: low gross, Paul A. Dunkel, 76, cup; nearest to pin on number 4 hole, J. E. Meili, 11′ 1″; kickers handicap, net score of 71, Patrick J. Kennedy, Milton K. Emerson, Emmett J. Driscoll, Lt. Roy G. Buck, J. L. Meltzer, A. J. Kellner, B. J. Tyler, Joseph E. Lange, Albert F. Johann. *Guests*: low gross, F. A. Murphy, 74; kickers handicap, net score of 74, H. B. Clark, N. Lufken, L. Zolla, E. Hinckler; kickers handicap, net score of 75, M. Lopez, A. Born, C. Greischel. *Special Events*: highest score for round, 155, G. Blasius; highest individual hole score, 12 on number 1 hole, J. Hintermaier.

Tennis—Award to Dan Finkel.

Horseshoes—Awards to Mr. Staek, Charles Pruiskma, Werner von Bergen, Mr. Manning.

The committee for the outing consisted of Paul J. Luck, chairman; Henry F. Herrmann, golf; Robert F. Holoch, horseshoes; Herman P. Baumann, tennis; and E. H. Schmidt.

Respectfully submitted,

NORMAN A. JOHNSON,
Secretary.

ANNUAL OUTING
NEW YORK SECTION
North Jersey Country Club
June 19, 1942

Photos by
Werner von Bergen and N. A. Johnson

MEMBERS IN ARMED SERVICES

THE following are reported in the Armed Services of the United States. The list is necessarily incomplete, and the Secretary will appreciate additions or corrections:

Richard Abrahams
Louis E. Anderson, Jr.
Paul Otey Anderson, Jr.
Robert C. Andrews
Stanley Backer
J. E. Barnhill
Charles E. Bergamini
G. Harold Best
Ion M. Bethel
William F. Black
Andrew F. Blackburn
Joseph H. Boulanger
John Boyko
Stanley W. Brown
George Brownlee, Jr.
Roy G. Buck
Donald Y. Buckingham
A. B. Bullington
Robert C. Carr
William L. Carter
Arthur S. Davis
John P. Dougherty
Eugene H. Driver
Lane C. Drye
William A. Drummond
Edward J. Epstein
John A. Feifer
Kirk P. Ferguson
Saunder Finard
L. A. Fiori
Clifford P. Flanagan
George E. Fogle
Stephen K. Ford
Julian C. Freel
Frank B. Gill
T. S. Greenwood
W. T. Gregory
Charles B. Griffin
Edmund D. Griffin, Jr.
Abraham H. Grondin
Clinton Grossman
Clarence Hooper
C. Fletcher Horn
Ralph C. Horner
Kenneth E. Leslie
Jack R. Luick
Edward J. F. Maslanka
Thomas H. McCamy
Charles P. McCann
Gannt W. Miller
Elliot Morrill
James M. Mozley
Max E. Nestler
Andrew F. Nuttall
Norman H. Nuttall
Herbert C. Olsen
James H. Parechanian
P. M. Parrott
William S. Pearson
Alfred H. Peel
Arthur W. Powell
Walter F. Prien
Raleigh V. Reece
Sidney I. Reichart
Robert K. Remer
N. B. Ritchie
L. H. Roane
Angus H. Roberts
Hillary Robinette
Henry J. Rotters
Sidney I. Saltsman
Ernesto V. Santos
T. J. Sarandria
J. E. A. Schroeder
Robert G. Schwarz
Walter M. Scott
Fred R. Sheldon
Charles L. Shelton
James C. Shore
Paul Lester Shurr
Basil G. Skalkeas
W. Douglas Smith
Edward Spevack
F. N. Spoerl
Charles A. Spratt
Frank M. Steadman
Harold W. Stiegler
Ross M. Stribling
Sanford L. Hornung
James T. Howes
Robert M. Hughes, Jr.
Walker Cobb Hunter
Bernard C. Jackson
Frederick D. Jones
Lewis T. Kelly
David H. Kennemur
Hulett L. King
Maurice King
Carl W. Kuhl, 2nd.
Henry H. Latham
Frank J. Szymosek
Robert M. Tarrant
S. P. Taylor
John P. Thornton
Daniel A. Torrence
Kelly E. Traynham
William H. Wadsworth
H. A. Webb
Henry A. Wells
Walter D. Worth
J. B. Wray
Roy J. Ziegler

MEETING, SOUTH CENTRAL SECTION

THE June meeting of the South Central Section was held Saturday night, June 27th, at the Read House in Chattanooga, Tennessee, with approximately forty members and guests present.

Two moving pictures were presented. "Threads of a Nation" produced by the Cotton Textile Institute in Technicolor, and "Civilization Fabrics" produced by Fruit of the Looms Company.

George S. McCarty was elected secretary to complete the unexpired term of Dan Torrence, who is now serving with the armed forces.

Because of transportation difficulties it was decided not to hold the annual summer outing.

Respectfully submitted,

GEORGE S. MCCARTY, *Secretary.*

ANNUAL OUTING, MID-WEST SECTION

THE Twelfth Annual Meeting and Outing of the Mid-West Section was held at the Lake Lawn Hotel, Lake Delavan, Wisconsin, on June 13th, 1942.

The Outing Committee, headed by A. T. Brainerd, did all that was possible to make this a memorable occasion, but the weather man fought back with a vicious ferocity.

The outing was attended by sixty-three members and thirty-eight guests.

The morning soft ball game was won by the Dyers with a score of 12 to 6 over the Salesmen.

Very creditable golf scores were turned in during the afternoon in spite of the rain and cold northwest wind. Winners were as follows:

Low Gross Cup—E. F. Smith.
Low Gross Mill Men's Trophy—Tied: A. Rathke, K. Harms. Won by K. Harms.
Low Net Mill Men's Trophy—G. R. Kremers.
Low Gross Guests—R. D. Totten.
Low Net Guests—R. H. Smith.

Respectfully submitted,

J. R. STOTT, *Secretary.*

TRADE NOTES • NEW PRODUCTS

• NEW ULTRA-VIOLET UNIT

Pfaltz & Bauer, Inc., Empire State Bldg., New York, are currently offering a new pure fused quartz ultra-violet generator of high efficiency and high intensity. This unit is specifically designed for the textile industry for exposure and fading tests, the study of rayons, wools, cottons, etc., detection of different dyes, damaged materials, dye blemishes and effects of washing. Complete information on this unit is available by addressing Pfaltz & Bauer, Inc.

• ABSORBS SUDITE CHEMICAL

The Tesco Chemical Co. of Atlanta, Ga., has recently absorbed the Sudite Chemical Manufacturing Co. of the same city. Sudite is a producer of cold water soaps, cleaning compounds and automotive specialties. For the time being, operations of the Sudite plant will be continued. With the completion of a new extension, the machinery and equipment will be transferred to the Tesco plant.

• FABRIC RESEARCH LABORATORIES

Fabric Research Laboratories, Inc., have recently been organized with offices at 665 Boylston St., Boston, Mass. They state that they have facilities available for research, testing and consulting for the textile and allied industries. Officers are: E. R. Kaswell, President; W. J. Hamburger, Treasurer, and K. R. Fox, Consultant.

• NOPCO COMPLETE SOAP

It is stated that modern washing technique has resulted in the development of a "complete soap" whose introduction is rapidly supplanting the "rule of thumb" method of mixing soap and alkali.

Research chemists of the National Oil Products Company have evolved a compounded mixture of anhydrous soap and a series of especially selected alkalies to which have been added solvents and penetrants.

Nopco Complete Soap was prepared for use by launderers of commercial and institional work where maximum cleanliness, whiteness and clean odor are essential. It is said to possess a uniform balance of alkali and soap plus the advantages of solvent action and penetration.

Its advantages are said to include greater detergency because of superior soil-removing power; sufficient suspending ability to insure the retention of foreign matter so that it is easily carried away in the rinse; quick rinsing to save time and assure clean, odorless whites and fresh, bright colors, and specially selected penetrants insure the utmost stain removal with a minimum of bleach.

• GENERAL ANILINE CHEMICAL DIRECTOR

The appointment of Dr. Evan Clifford Williams, international research chemist and chemical engineer, as Chemical Director and Vice-President of General Aniline & Film Corporation and his election to the Board of Directors was made known recently.

DR. E. C. WILLIAMS

Announced as an important step in rounding out the organization of General Aniline & Film Corporation, Dr. Williams' appointment is expected to strengthen the company's participation in the war effort and expand activities in its research division.

The stock of General Aniline & Film has been vested in Leo T. Crowley, Alien Property Custodian of the United States.

Before the war, the Corporation had the advantage of the research activities of the I. G. Farben organization in Germany. With this no longer available, Dr. Williams will have the responsibility of developing a laboratory organization competent to function in its stead.

With Dr. W. F. Zimmerli, Vice-President in Charge of Patents and Research, and other outstanding technical men recently added to the staff of General Aniline, it is felt that the laboratory will soon occupy a high place among the research organizations of the American Chemical Industry.

• COORDINATED WAR EFFORT

Interchemical Corp. has organized the technical and sales staffs of all of its divisions and subsidiaries in a coordinated effort to make its varied and comprehensive plant equipment available for war work. Each division was requested to analyze and report on its production facilities and to list the war products it was making. These facts from each subsidiary were compiled, edited and published in a "Manual of Products."

A series of sales oranization meetings was held in the major territories, at which, for the first time, salesmen from all of Interchemical's divisions and subsidiaries sat down to plan together for an all out war business program.

The products of Interchemical, its divisions and subsidiary companies constitute a great volume of production in the protective and decorative chemical coating industry. One of these companies alone is said to produce 85 different protective coatings which are now used on war machines and equipment.

Heretofore each company in the corporate set-up has confined itself to its own particular field of operations. As a result of the "Manual of Products" and of the sales meetings, every salesman is equipped to tell what each division of Interchemical is doing and what each division can make.

The "Manual of Products" was distributed to employees of Interchemical and is available outside the company only to governmental bureaus and other authorized purchasing personnel.

• McCAIN RETIRES

Retirement of Brigadier General William A. McCain, Commanding General of the Philadelphia Quartermaster Depot since 1934, was announced recently by the War Department. The order became effective June 30.

General McCain has been in military service for more than 40 years and was awarded the Distinguished Service Medal for "exceptionally meritorious and distinguished" service in operations during the St. Mihiel and Meuse-Argonne offensives in 1918.

Colonel Robert C. Brady, the depot's Executive Officer, has been placed in command. Formerly, Colonel Brady has been successively in charge of the depot's warehousing division, assistant commandant of the General Administrative School, property officer, and in charge of the Storage and Distribution Division.

• CONTROL OF DISTRIBUTION OF ANILINE

Control of the distribution of aniline, important chemical in the manufacture of explosives, dyes, drugs, synthetic rubber and other chemical products, was taken on July 13th by the Director-General for Operations, WPB.

Consumers seeking delivery of aniline under Order M-184, which was issued on July 13th, must file requests on Form PD-583 and producers and distributors must report monthly on Form PD-584. The Army, Navy, Coast Guard, Maritime Com-

mission and War Shipping Administration need not file these forms, but must provide the same information in any form they desire. Requests must be filed by August 10th for September delivery.

The restrictions of the order do not apply to use by the Armed Services of aniline produced by them, or to the use by any person of less than 500 pounds of aniline in a month.

Consumers requesting 500 pounds or less in a month must certify to the shipper that the total they receive from all shippers will not be more than 500 pounds. Deliveries of 50 pounds or less are not subject to certification.

While no shortage of aniline exists at present, increasing demand and possible interruption of imports make the control advisable.

• SALVAGE COMMITTEE

Formation of the American Industries Salvage Committee, representing groups of leading industrial concerns who are working with the Conservation Division of the War Production Board to help speed the collection of vital scrap materials, has been announced by Robert W. Wolcott, Chairman of the group and President of Lukens Steel Company.

Other members of the administrative committee directing the nationwide $2,000,000 campaign are: Charles R. Hook, President of the American Rolling Mill Company, Vice Chairman; R. S. Wilson, representing Rubber Manufacturers Association; and O. E. Mount, representing Steel Founders' Society of America.

The work of the committee, backing up a broad advertising program, will be twofold: 1, to reach every manufacturing and business firm in the nation to impress upon them the absolute necessity of getting their scrap on the way to the production line; and, 2, to get business men cooperating with the local salvage committee of WPB already set up in 12,000 communities.

The activities of the committee will be closely coordinated with the present intensified scrap collection drive of the WPB, according to Mr. Wolcott. In this connection, the committee is underwriting the cost of an extensive national advertising campaign approved by the War Production Board, with a number of major industries underwriting the costs.

The advertising being carried on in newspapers, magazines, farm and trade papers and on the air, focuses the spotlight of public attention upon the need for iron and steel scrap, non-ferrous metals, rags, burlap, rubber, tin cans (in some localities), and waste cooking fats.

Supplementing contracts with industry already established by the Industrial Salvage division of WPB, the American Industries Salvage Committee will make a direct approach to individual industrial concerns, working through industry chairmen who are now being appointed. Leaders in 50 industries are being asked to serve as chairmen for their respective trades in a broad effort to see that every company appoints a salvage manager with authority not only to clean out production scrap, but also to junk obsolescent equipment and similar material.

• NEW YORK OFFICES, WARWICK CHEMICAL

Members of the Warwick Chemical Company recently celebrated their moving to new and larger offices at 580 Fifth Ave., New York City. At the party, Ernest Nathan, President, expressed his gratitude to the members of the organization for their cooperation in making the rising success of the company possible. The phone number and address remain the same.

• CALCO BULLETINS

The textile trade in general will be interested in the announcement from Calco Chemical Division, American Cyanamid Company, that a new bulletin on "Military Shades on Cotton Thread Vat Dyed on Packages by the Pigment Method" has just been released.

This bulletin contains a review of Federal Specificaiton V-T-276b of December 30, 1937, and its requirements, and thereinafter lists a series of dyeing procedures supported by formulae and samplings on various weights of cotton thread.

The shades covered in Calco Technical Bulletin No. 650 are Khaki, Olive Drab, Olive Drab No. 3, Olive Drab Shade 258, Olive Drab Wind Resistant Poplin, Light Olive Drab for Worsted, Dark Olive Drab for Worsted, Powder Blue Nurses' Broadcloth—Type II and Blue Nurses' Uniform—Seersucker.

The "Dyeing of Olive Drab No. 3 and No. 22 Shades with Sulphur and Vat Dyes on Cotton Yarn for Webbing" is discussed extensively in another new bulletin just issued by Calco.

This bulletin contains a transcription of U. S. Army Specification No. 6-185C, October 1, 1941, in addition to a comprehensive discussion of formulae and procedure for dyeing shades by package, cascade and hand tub methods. The information contained in Calco Technical Bulletin No. 646 is supported by samples of the dyeings on 16's/2 ply and 10's/5 ply yarn.

Copies of both bulletins may be had by addressing the Advertising Department, Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

• RESEARCH ON NICKEL

The International Nickel Company, Inc., New York, N. Y., has resumed investigational work at Mellon Institute of Industrial Research, Pittsburgh, Pa., by the establishment of an Industrial Fellowship that began operation on July 1. This Fellowship is concerned with a comprehensive program of scientific research on certain problems in the chemistry and technology of nickel, embracing particular attention to the preparation, properties, and uses of nickel compounds, especially organic derivatives.

Dr. John Gilbert Dean, a physico-organic chemist, is the incumbent of this Fellowship. He received his professional education at Brown University (Ph.B., 1931; M.S., 1932) and Columbia University (Ph.D., 1936) and has subsequently had five years of experience in applied chemical research.

• NEW DATES AND LOCATION FOR CHEMICAL EXPOSITION

Announcement is made by the Chicago Section of the American Chemical Society of a change in dates and location for its second National Chemical Exposition, owing to the acquisition of the Stevens Hotel in Chicago by the United States Army.

The exposition and conference have been transferred to the Sherman Hotel, conveniently located in the Chicago business center at Clark and Randolph Sts., and will take place from November 24 to 29 instead of a week earlier as originally planned.

"Adequate space will be available for a show about twice at large as the first exposition sponsored by the Chicago Section in 1940 and under most advantageous conditions," said Victor Conquest, chairman of the show committee.

"Our preliminary survey indicates that we can accommodate more than 100 exhibitors. Just how many in excess of that number we can take care of is a question at this time. Our original plan provided spaces for 145 exhibitors. It is important, therefore, that all who plan to exhibit in this important war-time show file application for space at once."

No changes are planned in the original program for the show, it is announced. There will be daily conferences to be addressed by leaders in the chemical industry, educators and other outstanding authorities. The committee is arranging for an interesting display of motion pictures. Adequate accommodations will be available in the Sherman Hotel for the thousands of visitors expected from all over the country.

Mr. Conquest points out that the importance of the show cannot be underestimated. The chemical industry is vital in the war effort. Many new processes and discoveries will be revealed. The exposition will offer the opportunity to exchange ideas and to view latest developments in an industry which has contracts for construction projects totaling $72,118,000 this year as compared with $46,996,000 a year ago.

OBITUARY

HENRY KOOPMAN

HENRY KOOPMAN, manager of sales for the Chemical Corporation of America, Paterson, N. J., died in New York City on July 10th, 1942. He was 32 years of age.

Mr. Koopman was a graduate of Columbia University and, since his graduation, had varied experience in the textile field. For the past five years he had been in charge of sales and the technical department of the Chemical Corporation of America. He was a member of the New York Section of the American Association of Textile Chemists and Colorists.

He is survived by his wife and a two months old daughter.

• EASTON LABORATORY, GENERAL ANILINE

General Aniline & Film Corporation announced recently that it had leased a four-story building in South Easton, Pennsylvania, which will at once be remodeled for use as a central research laboratory for the Corporation. The leased building is a reinforced concrete structure formerly operated as one of the plants of the Stewart Silk Corporation. A number of General Aniline's research men working in the chemical field will be transferred from operating plants of the company to the new Easton laboratory and their number will be augmented by other chemists.

Due to its pre-war affiliation with I. G. Farben, the German dye trust, control of the Corporation is now vested in Leo T. Crowley, Alien Property Custodian.

• PRODUCTION OF DUPONT MATERIALS

Production of DuPont material required for the war emergency, whether of chemicals or explosives, is at an all-time high, Walter S. Carpenter, Jr., president of E. I. du Pont de Nemours and Company, announced in a statement to stockholders recently.

Plant expansion on an unprecedented scale, largely constructed and operated for the account of the Government, has involved expenditures totaling several hundred millions of dollars, he said. Every construction project has been completed in advance of contract schedules, and similarly, all production schedules have been met or exceeded.

The six months period just ended has marked the practical completion of a significant transition, Mr. Carpenter stated, to satisfy the imperative requirements of the military and the essential civilian needs of a nation at war. In contrast with manufacturers today, sales of military products for the 20-year period prior to the present war constituted less than two per cent of the total, with approximately 98 per cent chemical products to meet the normal peacetime needs of the people.

Pointing out that Du Pont's neoprene was the first so-called synthetic rubber to be produced on a commercial scale, he noted that the company began its manufacture a decade ago and that since then production has been increased steadily.

Nylon production has likewise been expanded rapidly, Mr. Carpenter stated. The capacity of the original plant has been doubled and a further new plant has gone into production.

The major portion of all vat colors used for military and naval purposes are being made by Du Pont, Mr. Carpenter said, with this country now "self-sufficient in all of its essential dye requirements."

"Cordura" rayon yarn has been adapted to use in tires for heavy duty on airplanes and mechanized military equipment, and is said to increase both strength and durability, thus contributing to conservation of rubber.

Production of cast transparent sheets of "Lucite," used in military airplane construction, has reached new high levels. The output during the last six months has been nearly quadruple that for the comparable period of 1941.

Output of nitrogen extracted from the air likewise has been substantially expanded. Speed of construction of powder plants and production in plants already in operation have exceeded expectations. Improvements in manufacture and technique have contributed to this achievement. Each TNT unit of production, Mr. Carpenter declared, "is now turning out three times the quantity that similar units were able to produce during the first World War."

"These are only a few of the items which might be listed as contributing to the prosecution of the war," said Mr. Carpenter. "It is interesting to observe that many of them are chemical achievements which have come into being since the first World War. Furthermore, just as this company's laboratories have developed new products in peace-time to improve our conditions of living, so now, with temporarily changed aims and endeavors, new war developments have commenced to flow from these same laboratories."

COMMUNICATION
Re Sulfur Colors

23rd May, 1942.

To the Editor,
American Dyestuff Reporter.
Dear Sir:

Much space is given in *The Dyer,* of May 15th, 1942, to a paper presented at a meeting of the Piedmont Section, A.A.T.C.C., by John L. Crist, and printed in your Reporter, entitled:—

THE PLACE OF SULFUR COLORS IN WAR PRODUCTION.

The extract of this paper printed in *The Dyer,* deals with the relative costs and merits of sulfur dyeing as compared with vat dyeing. The facts stated, together with the saving of chemicals (necessary for war) which are required in the manufacture of vat dyes, as well as in their application, are most important and instructive.

Sulfur dyed cotton goods costing 1/7th to 1/12th of the amount for dyeing the same shades in vat colors, and with a 75 per cent fastness quality result, is mentioned by Mr. Crist. The object of the paper is apparently:

(a) Saving of chemicals essential to war,
(b) Giving a cloth quite good for general purposes, at a very much lower dyeing cost than vat, although not as fast.

Quoting from the paper, "1 pound of toluene will produce sufficient sulfur khaki dyestuff to dye 600 lbs. of cotton to the Army O.D.3 shade, or 2,400 yards of four-yard goods." It would be interesting to know how the actual cost to the dyer, in materials and labor, of dyeing the aforenamed 2,400 yards of cotton goods in sulfur khaki, compare with the cost in materials and labor, of dyeing the same shade in mineral khaki. This comparison is best made on the local ground which witnessed the sulfur costing, as prices and conditions generally in Piedmont, will be widely different from those of Manchester. It will be found, however, in the opinion of the writer, that the mineral khaki costing is even lower than the sulfur khaki costing, and has the advantage of being 100 per cent fast. It may be found, however, that the amount of chemicals (necessary for war) used in making the chrome and iron liquors for mineral, is greater than in the case of sulfur.

Perhaps Mr. Crist, and the gentlemen referred to in

the paper, have already made this test of comparison between sulfur and mineral, in relation to war materials necessary, and costs of respective methods of dyeing. If not, the subject might be worth probing into, presuming that a mineral khaki plant is convenient, which uses liquors made on the premises, from sodium bichromate, hydrochloric acid, calcium acetate, and ferrous sulfate.

Or again, Mr. Crist may be engaged in the manufacture of dyestuffs, in which case mineral khaki dyeing will be of no interest to him. Thanks to Mr. Crist, and the "American Dyestuff Reporter," for a very interesting and instructive paper.

Yours truly,

A. STOCKS, *Greenhills, Drogheda, Eire.*

ELASTICITY OF WOOL

(Continued from page 380)

ess[39, 18], it appears that proof of the chemical structure of the cross-links is lacking. On the other hand, it now seems well established that in wool the disulfide groups of the amino acid cystine do form cross-links between molecular chains. Thus, the difference in behavior of wools, before and after rupturing these cross-links serves as a useful model for rubber, and indeed, as is seen in the following discussion, lends considerable support to the hypothesis of cross-linking in vulcanized rubber.

A consideration of the chemistry of the wool fiber during the course of its production brings forth some additional points relative to this discussion. A growing wool fiber consists of a root and a shaft, the former being the living region situated beneath the surface of the skin whereas the latter is the non-living portion extending above the surface. Examination of the root portion reveals that it is principally a gelatinous protein mass containing a relatively large amount of sulfhydryl groups[16]. In other words, it would appear that in the synthesis of wool, cysteine rather than cystine, is synthesized into the polypeptide chains. The material in the root of the hair is in some ways comparable to rubber latex. When the hair cells die, oxidation presumably takes place since the sulfhydryl groups are completely converted to disulfide groups. At this stage, the soft, plastic material of the root becomes the tough, elastic wool fiber. This, in a sense, can be considered to be analogous to the vulcanization process.

The solubility and swelling properties of both wool and rubber serve to emphasize the similarity in the physical structures of these two materials. Untreated wool fibers swell appreciably in a variety of aqueous solutions but are definitely insoluble in the usual protein solvents. Rupture of the disulfide cross-links yields a product which is readily soluble, for example, in alkaline solutions, but the original insolubility is restored after re-formation of these links[28]. Similarly it can be shown that whereas unvulcanized rubber is soluble in a variety of organic solvents, vulcanization renders the material insoluble in the same solvents. With unvulcanized rubber, it is possible to form a clear solution of the rubber in a solvent, but the vulcanized rubber appears only to swell and form a gel-like structure[10].

Since, in the absence of imposed strain, neither material exists in the fully extended form, there can be little close packing and accordingly there will be relatively few points of interaction as compared with highly oriented materials such as the cellulose, silk, or nylon fibers. As would be expected, the tensile strengths, or, more generally, the resistance to further extension, of such normally unoriented materials is always low. Within the range from zero strength to these low maxima, however, resistance to extension is sensitively related to the frequency and intensity of molecular interactions. This is readily demonstrated by the stress-strain behavior of unvulcanized rubber, or of wool in which practically all of the disulfide cross-linkages have been ruptured. However, when rubber is vulcanized or the cross-links are introduced into reduced wool, similar changes in the mechanical properties of both materials are observed, as shown in Figures 2 and 6. It is seen that with cross-linking the materials become stronger, and their moduli of elasticity become higher. In addition, they show lower extensibilities at break. Modified wool fibers in which the cross-links have been ruptured may be stretched in water more than 100 per cent before breaking, whereas untreated wool fibers show extensibilities of only 50 to 60 per cent. A representative sample of unvulcanized rubber had an elongation of 1200 per cent at break, whereas after vulcanization the elongation at break of a similar sample was only 700 per cent[29].

There is, however, one principal difference between the two types of molecules. Rubber is practically entirely hydrocarbon and accordingly exhibits only low-order molecular cohesion or interactions whereas wool contains a large proportion of highly polar groups capable of forming relatively strong molecular interactions. For this reason, the sensitivity of rubber to temperature is not shared by dry wool. On the other hand, the mechanical properties of the latter are greatly affected by moisture, which swells the protein and presumably decreases intermolecular cohesion. Thus, it is found that the influence of heat on the mechanical behavior of rubber is very similar to the influence of moisture on the behavior of wool.

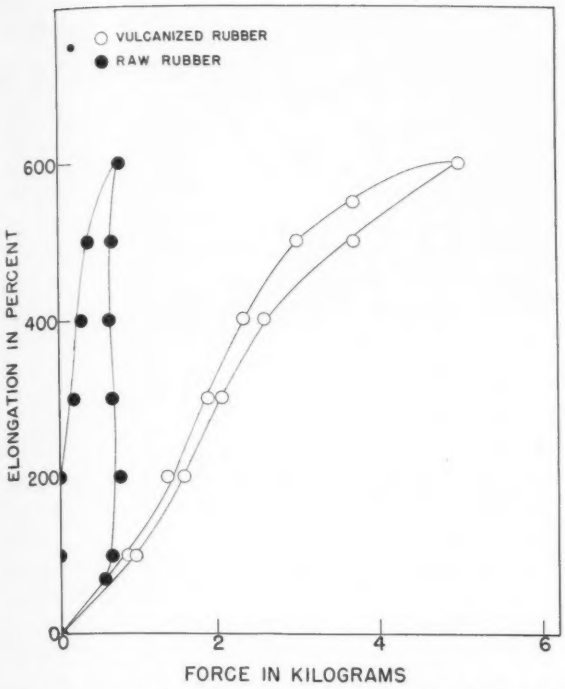


Fig. 6—Stress-strain cycles of a sample of rubber, before and after vulcanization. Data from Hock and Bostroem[17].

VI. CONCLUSION

These experiments and comparisons lead to a better understanding of the molecular basis of the elastic properties of wool. The long-range elastic characteristics are not dependent on the presence of cross-links but probably result from the ability of flexible chain molecules to contract from the less probable stretched state to a more random form. Meyer[25] and Mark[21] have reviewed the evidence for this view of the origin of long-range elasticity. The function of cross-links is to strengthen the materials and suppress plastic flow. The introduction of a higher proportion of cross-links would decrease the flexibility and reduce the range of elasticity, as illustrated by the properties of highly vulcanized rubber (ebonite). This analysis of the mechanical properties of these systems leads to the conclusion that a textile fiber having desirable long-range elastic characteristics must consist of flexible chains reinforced with a proper balance of cross-links.*

The influence of covalent chemical cross-linking on the properties of wool, rubber, and other high-polymer systems is now receiving considerable attention. As far as the authors are aware, wool is not only the first substance in which covalent cross-linking has been established, but also is the only one in which the cross-links can be quantitatively ruptured and rebuilt at will. It may thus serve as an excellent model for many other high-polymeric systems.

*In this connection, it is interesting to note that the absence of any appreciable amount of covalent cross-linkings undoubtedly accounts to a large extent for the low tensile strengths, especially in the wet state, of regenerated protein fibers made from casein, soybean protein, etc. Silk fibers, on the other hand, which apparently do not contain any covalent cross-linking exhibit very high tensile strengths. Examination of their chemical constitutions reveals that nearly two-thirds of the amino acid content is accounted for by glycine and alanine, compounds which have only hydrogen and methyl groups as side chains[5]. From the available analytical figures, with the further assumption that the nitrogen not accounted for is all peptide chain nitrogen, it is found that only 36 per cent of the weight of silk is in the side chains, in contrast to 48 per cent for wool and 54 per cent for casein. It follows that while in wool the chain weight is to the side chain as 1 to 1, in silk this ratio is nearly 2 to 1. Polypeptide chains of silk may thus be considered to be significantly more bare than those of wool, making possible a considerable amount of close packing and interchain hydrogen bonding, which would account for the high observed strengths. Comparison of the X-ray diagrams of silk and of wool[2] shows a much higher "degree of crystallization" in the silk.

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Chemistry of Fibers—

(Continued from page 375)

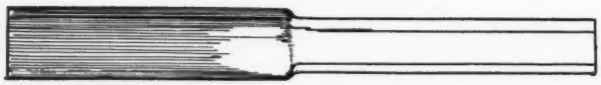

Fig. 5—Cold Drawing of Polyester Fiber

and smoothly, and it led to oriented fibers of uniform cross sections. The oriented and unoriented forms of the polyester were different crystalline states and in the cold drawing operation one crystalline form, was instantly transformed into the other, merely by the action of very slight mechanical stress.

After drawing, the thin transparent fibers were found to be strong and pliable. Rough determinations indicated that the oriented transparent filaments prepared by cold drawing were six times greater in breaking strength than the partially oriented opaque undrawn filaments. This "cold drawing" process is an important phase in the preparation of nylon today.

Carothers found that the property of cold drawing did not appear in the polyesters until the molecular weight reached 9,000. He concluded that a useful degree of strength and pliability in a fiber required a molecular weight of at least 12,000 and a molecular length of not less than 1,000 Angstrom units.

It is interesting to note that the early patents (U. S. Patents 2,071,250, 2,071,251, 2,071,252, 2,071,253) granted to Carothers covered, in part, the production of polyamides from the condensation of an amine and a dibasic acid, which reaction, we believe, is followed in the present production of nylon. This condensation has hardly been touched upon in Carothers' "Collected Papers."

We feel that it would be wasted effort to review the reactions whereby polyamides may be produced. These have been described with great clarity and completeness by Carothers in his patent applications. There is one statement, however, which this eminent scientist made regarding polymerization which we quote herewith. This should serve as an axiom for those who follow him. This attitude, apparently, prevailed in all of Carothers' work:

"Our researches on condensation polymers were started with the idea that the fact of a proposed model's being synthetic is of little value, unless the method is rational, i.e., unless it is sufficiently clear-cut to leave no doubt concerning the structure of the product."

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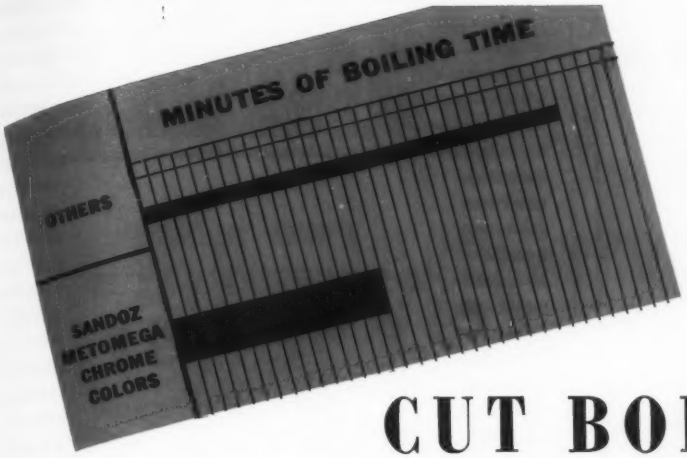

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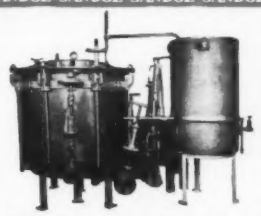

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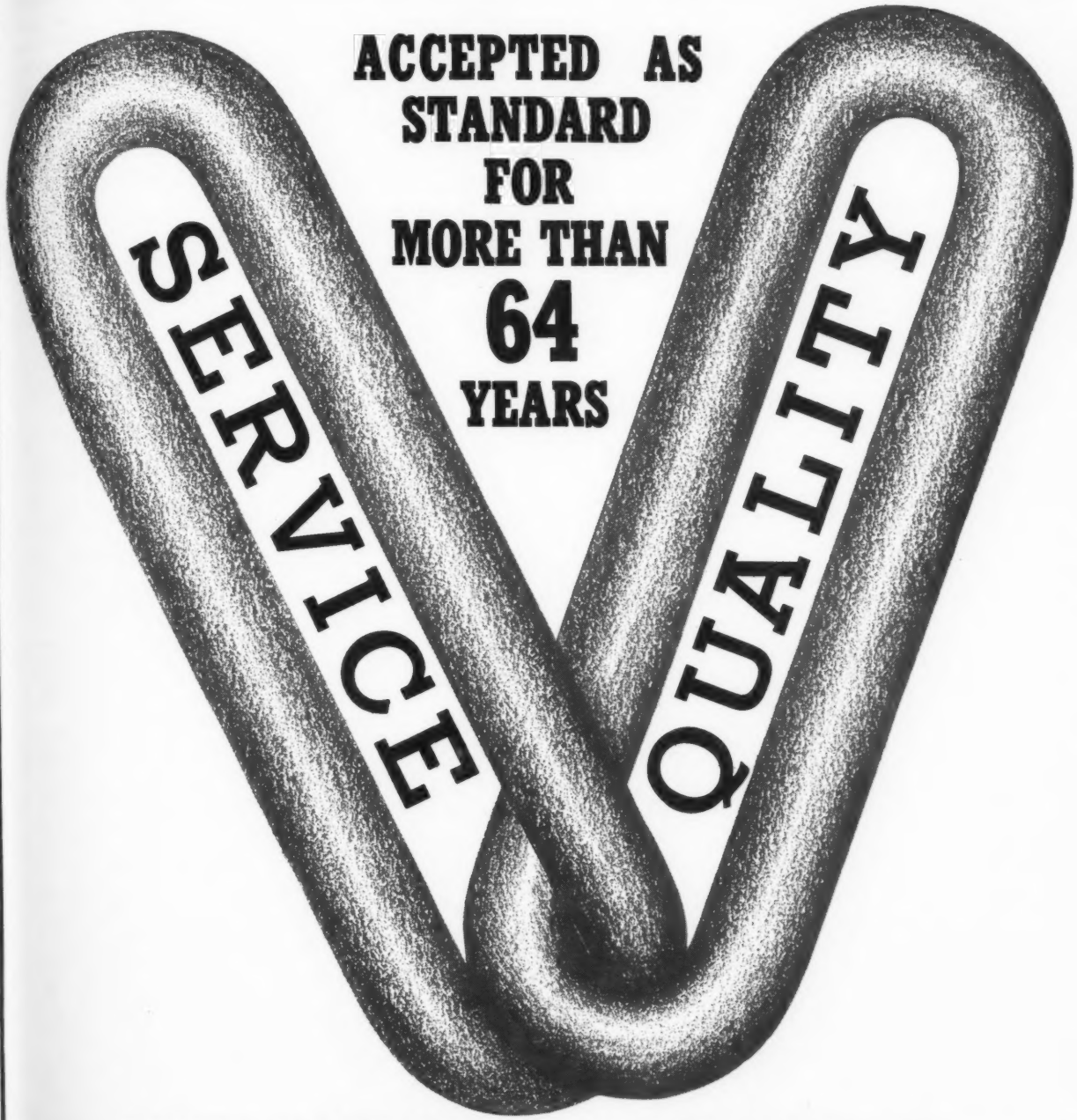

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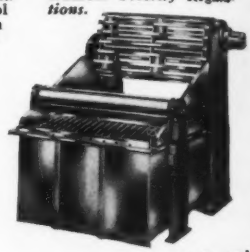

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for Acetate Rayons

Very brilliant as a self shade and suitable as a base for bright greens.

Remarkable for its building up properties and its fastness to rubbing in heavy shades.

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ESTABLISHED 1897

Manufacturing Chemists

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—for accelerated washing tests

Standard laboratory washing machines of the A.A.T.C.C.—measures resistance to washing action, shrinking, staining, color fastness to soaps and solvents. All factors, including washing action, carefully controlled—can be reproduced exactly at any time.

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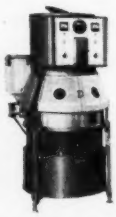

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—for accelerated weathering tests

Duplicates effect of actual exposure—months of sun, rain, heat, and cold condensed to a few days.

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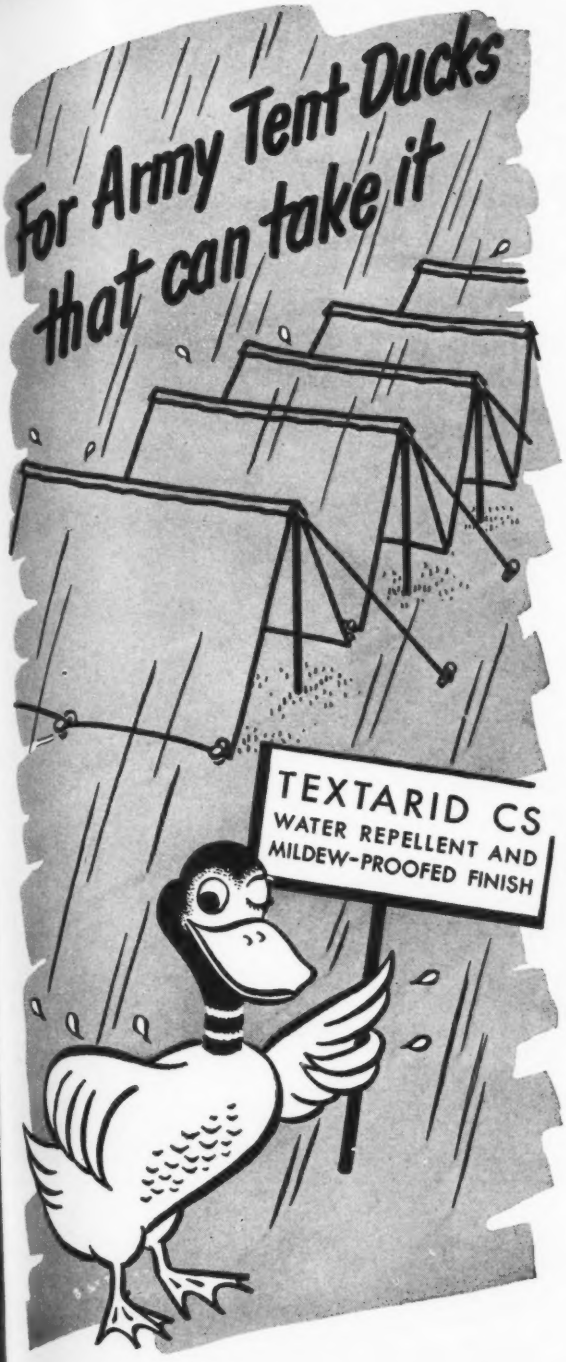

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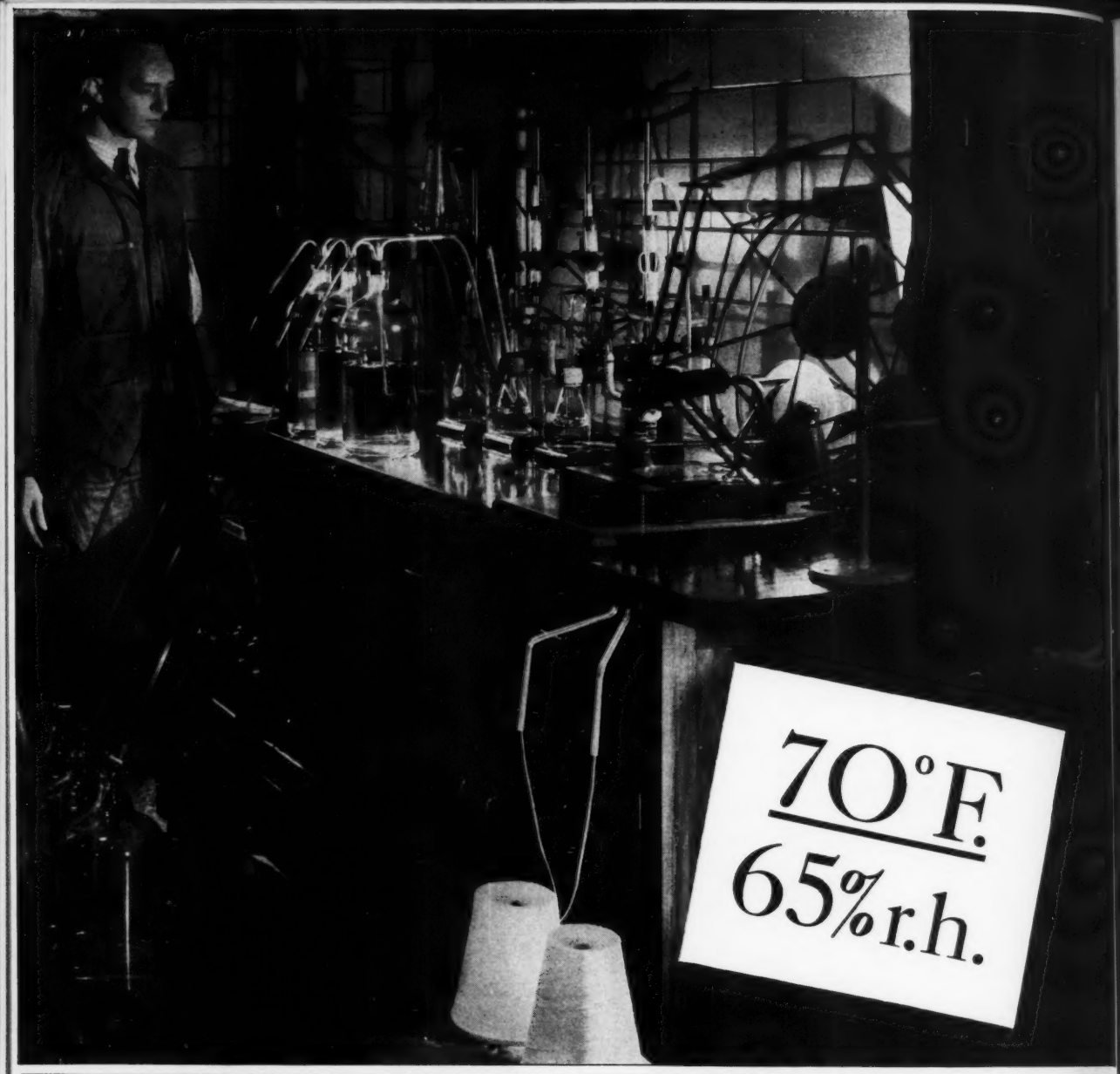

EVALUATION LABORATORY — The photograph shows one corner of the Rohm & Haas Textile Evaluation Laboratory where new products are tested, fabric treatments evaluated, and new testing methods developed. In the background is a control board which automatically maintains in the laboratory a constant temperature of 70°F. and a relative humidity of 65%. The highlighted laboratory equipment was designed by the Evaluation Laboratory to determine and evaluate the hygroscopic properties of new resins and sizes. An accurately measured volume of saturated air is passed over the dried samples to determine the moisture pick-up. Other equipment in the photograph includes an abrasion tester, a skein winder, and equipment for the Draves Test.

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Whenever there is a standard device for testing specific properties, such a machine will almost always be available in the Rohm & Haas Laboratories. In cases when no standard testing device is available, Rohm & Haas research men have developed devices for accomplishing the desired result.

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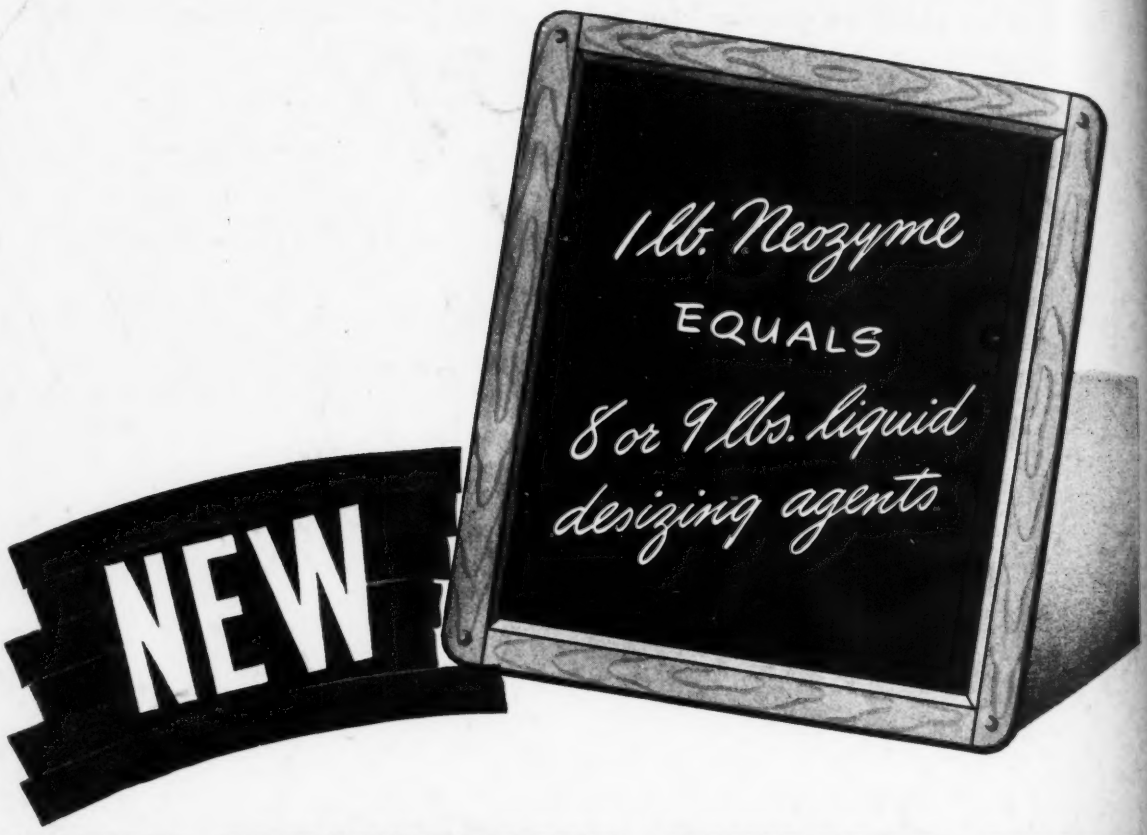

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